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THE METALLIC DERIVATIVES OF ACETYLENE.

BY EDWARD H. KEISER.

In a previous paper[1] it was shown that the explosive compounds obtained by the action of acetylene upon ammoniacal solutions of cuprous chloride and silver nitrate have the composition represented by the formulas C_2Cu_2 and C_2Ag_2, and that they are to be regarded as metallic substitution-products of this hydrocarbon. The work upon the metallic derivatives of acetylene has been continued, and a study has now been made of the action of the hydrocarbon upon aqueous and alkaline solutions of mercuric salts. When acetylene acts upon cuprous and silver salts the compounds Cu_2C_2 and Ag_2C_2 are formed both in aqueous and ammoniacal solutions. In the case of the mercuric salts, however, the action is different in aqueous from what it is in alkaline solution. Thus, when acetylene is conducted into a water solution of corrosive sublimate, a white granular precipitate is obtained which when dry is not explosive, and which does not dissolve in dilute acids with the evolution of acetylene. On the other hand, if the acetylene is passed into an alkaline mercuric solution—for example, a solution of mercuric iodide in potassium iodide to which caustic potash has been added—then a white flocculent precipitate is obtained. This precipitate when dry is extremely explosive, and it dissolves in dilute hydrochloric acid with the evolution of acetylene. It is analogous in all its properties to the silver and copper compounds of acetylene, and like these it is a metallic substitution-

[1] This Journal **14**, 285.

product of the hydrocarbon. Its composition is represented by the formula C_2Hg. The compound formed in an aqueous solution of mercuric chloride contains chlorine. Its composition is perhaps best represented by the formula $C_2(HgCl)_2$, and it may be regarded as acetylene in which the two hydrogen atoms have been replaced by two univalent (HgCl) groups.

The only reference in chemical literature to the explosive mercury compound of acetylene appears to be an article by H. Bassett[1] in the Chemical News for 1869. This experimenter passed coal-gas through Nessler's reagent and obtained a considerable quantity of a bright yellow precipitate which, after drying, exploded slightly when heated. He obtained a purer substance by passing the products of the incomplete combustion of coal-gas through Nessler's solution. A precipitate of a pale yellow color was formed which exploded rather more violently than that first obtained. An analysis of the substance gave 70.24 per cent. mercury and 23.5 per cent. iodine. Bassett gave to it the formula $C_2HHgI + HgO$.

In my earlier experiments it was found that the acetylene obtained by the incomplete combustion of coal-gas is mixed with so many other substances that pure silver and copper derivatives could not be obtained from it. For the preparation of the mercury compound the acetylene was made by the action of alcoholic potash upon ethylene bromide. The gas after leaving the generating-flask was passed through a solution of alcoholic potash heated on a water-bath, then it passed through two wash-bottles containing absolute alcohol and one containing water, and finally it was led into a solution of mercuric iodide in potassium iodide to which caustic potash had been added. A white flocculent precipitate was soon formed in large quantity. This was separated from the liquid by filtration, and was washed repeatedly with distilled water. The compound was then dried in desiccators over sulphuric acid. It does not, however, give up all its water in this way. It is only by prolonged heating upon the water-bath that it can be obtained entirely free from water. When it is heated to a higher temperature in an air-bath the compound gradually decomposes, the color becomes dark, and a vapor having an odor like that of phosphuretted hydrogen is given off. Apparently this decomposition begins at about 100°. Heated rapidly to a

[1] Chemical News **19**, 28.

somewhat higher temperature the compound explodes with extreme violence, finely divided carbon and mercury remaining behind. The compound contains no iodine. An analysis of the air-dried substance gave 83.11 per cent. mercury. After drying another portion of the same substance upon the water-bath until constant weight was obtained, a determination of mercury gave 88.9 per cent. The analysis was made by dissolving the weighed substance in dilute hydrochloric acid, precipitating the mercury as sulphide with hydrogen sulphide, and weighing the precipitate in a Gooch crucible after it had been dried until a constant weight was obtained.

Per cent. of Hg calculated for C_2Hg = 89.28.
Per cent. of Hg calculated for C_2Hg_2 = 94.33.
Per cent. of Hg calculated for $(C_2H)_2Hg$ = 80.00.
Found 88.94, 88.42 and 89.14.

The analysis of the substance, therefore, as well as its properties indicates that it is a true metallic substitution-product of acetylene. The formula being C_2Hg, the compound is especially interesting because in it both hydrogen atoms of the hydrocarbon are replaced by a single atom of a metal. Like the copper and silver compounds it dissolves readily in hydrochloric acid with the evolution of acetylene. A solution of mercuric chloride is thus obtained. When treated with an alcoholic solution of iodine it unites with the iodine slowly at ordinary temperatures, more rapidly at the temperature of the water-bath. Di-iodo-acetylene, C_2I_2, is thus formed. This, after standing some time, polymerizes and crystalline plates separate from the alcoholic solution. These crystals melt at 187° and are probably hexiodobenzene,[1] C_6I_6. This substance will be analyzed and studied more fully as soon as a larger quantity of it has been prepared.

Kutscherow[2] has studied the action of the acetylene hydrocarbons upon an aqueous solution of mercuric salts. He found that these hydrocarbons form non-explosive white precipitates, from which acids liberate addition-products of the hydrocarbons and water. Thus from acetylene aldehyde can be obtained, from allylene, acetone, from the higher members other ketones. He has not made any analyses of the compounds which acetylene forms with mercuric salts, his work having been mainly upon the allylene compounds. Analyses of the compound formed from

[1] See Baeyer: Ber. d. chem. Ges. **18**, 2276. [2] Ber. d. chem. Ges. **17**, 13.

allylene and an aqueous solution of corrosive sublimate led him to give this substance the formula $3HgCl_2.3HgO.2C_3H_4$, and he assigns to it a very complicated constitutional formula.

To obtain the acetylene compound the hydrocarbon, prepared as described above, was passed into a cold saturated solution of mercuric chloride. The solution soon became milky, and after a time a white granular precipitate settled to the bottom of the vessel. Hydrochloric acid is formed by this reaction. After a time the precipitation stops, although some mercury still remains in solution. The compound cannot be formed by passing acetylene through a solution of mercuric chloride in absolute ether. The precipitate was removed from the acid solution by filtration. It was washed first with water, then with alcohol, and finally with ether to ensure the removal of all mercuric chloride. It was then dried in desiccators over sulphuric acid. The compound was found to be insoluble in alcohol and ether, and was not acted upon by dilute hydrochloric acid. *Aqua regia* and fūming nitric acid dissolve it. The compound does not explode on heating, but if some of the dried substance be cautiously heated on a platinum spatula at a certain temperature it suddenly puffs up, forming a black porous mass, and white vapors are given off. If it is heated in a tube closed at one end a white sublimate of calomel, HgCl, is obtained and a porous mass of carbon remains behind. Like the explosive mercury acetylide this compound still retains some water after it has stood for a long time in the desiccator, and it is difficult to dry it in an air-bath without bringing about decomposition. Analyses of the compound after it had been dried in the desiccator gave results that agree fairly well with the formula $C_2(HgCl)_2.\frac{1}{2}H_2O$.

	Calculated.	Found.		
Hg	79.37	79.32	79.44	79.27
Cl	14.07	...	14.51	14.61
C	4.70	...	...	...
H_2O	1.86	...	1.63	1.74
	100.00			

Like the explosive mercury compound this one also unites with iodine, and from quantitative determinations one molecule of $C_2Hg_2Cl_2$ requires four atoms of iodine. This, taken in connection with the fact that, on heating, the compound is easily con-

verted into mercurous chloride and carbon, makes it seem probable that it is derived from acetylene by the replacement of the two hydrogen atoms by two HgCl groups. The equation of formation would then be:

$$C_2H_2 + 2HgCl_2 = 2HCl + C_2(HgCl)_2.$$

It is possible, however, that, when acetylene acts upon mercuric chloride, the compound C_2Hg is first formed, and that this unites immediately with a molecule of mercuric chloride, giving $C_2Hg_2Cl_2$.

The investigation of these and other metallic derivatives of acetylene will be continued.

In conclusion I desire to thank Miss E. H. Parker for valuable assistance given to me in making the experiments described in this paper.

BRYN MAWR, PA., *June*, 1893.

Contribution from the Chemical Laboratory of the Rose Polytechnic Institute.

VIII.—ON THE NITRITES OF SOME AMINES.

BY W. A. NOYES.

Some time since it was shown[1] that dibenzyl-carbinamine forms a nitrite which is stable in its aqueous solution at ordinary temperatures. A number of other amines have now been prepared for the purpose of studying the stability of their nitrites. The experiments to be described establish pretty conclusively that amines of the general formula $\frac{R}{R}>CHNH_2$ form nitrites which are stable at ordinary temperatures. No amine of this type has been found, however, which is not decomposed on boiling the concentrated aqueous solution of its nitrite. On the other hand it has been found that hexamethylene-diamine (1-4-diamino-cyclo-hexane) is not so stable toward nitrous acid as was formerly supposed; also that the nitrite of dihydro-meso-anthramine decomposes quite easily on boiling with water. It is worthy of note, also, that Semmler[2] has found that β-methyl-penta-methylene-amine (1-3-methyl-amino-cyclo-pentane) reacts normally toward nitrous acid,

[1] This Journal **14**, 225. [2] Ber. d. chem. Ges. **25**, 3519.

giving the corresponding alcohol. Wislicenus and König[1] have recently obtained oxyhydrinden, $C_6H_4<\begin{matrix}CH_2\\CH—OH\end{matrix}>CH_2$, by heating the chloride of amino-hydrindene with a solution of sodium nitrite.

Bamberger has recently expressed,[2] with some reserve, the opinion that the chemical character of completely hydrogenated ring systems is not dependent on the number of atoms included in the ring. If this be true, it must follow that, in their conduct toward nitrous acid, at least, there is no essential difference between alicyclic and aliphatic amines. The hydrogenated naphtyl amines studied by Bamberger and his co-workers are simply extreme cases, and the stability of their nitrites is not conditioned by the hydrogenated *ring*. Indeed Bamberger states that 1-2 phenyl-amino ethane[3] forms a nitrite which can be crystallized from boiling water. Apparently the chief factor in producing the strongly basic character of these amines and the stability of their nitrites is not the ring structure at all, but the accumulation of hydrogen in parts of the molecule which are in close proximity to the amine group.

Diethyl-carbinamine (*3-amino-pentane*).[4]

Diethyl-ketoxim was prepared by the method used by Scholl,[5] except that no alcohol was used. The diethyl-ketone with the solution of hydroxylamine chloride and sodium hydroxide were placed in a bottle and agitated for an hour by means of a turbine. The oxim was then removed from the solution with the aid of a little ether, the ethereal solution dried with calcium chloride and distilled till the thermometer rose to 150°. The portion remaining in the bulb was apparently the nearly pure oxim, and was reduced to the amine by means of absolute alcohol and sodium. The amine obtained was distilled from the alkaline solution in a current of steam; the distillate was collected in dilute hydrochloric acid and the solution evaporated to dryness. The conversion into the oxim and reduction to the amine appear to be nearly quantitative. This method of preparing amines seems to be of quite

[1] Ann. Chem. (Liebig) **275**, 350.

[2] Ber. d. chem. Ges. **26**, 1286.

[3] Ann. Chem. (Liebig) **257**, 19. The name given the compound by Dr. Bamberger would apply equally to the secondary amine derived from aniline.

[4] Communicated to the Chemical Section of the American Association for the Advancement of Science at the Rochester meeting.

[5] Ber. d. chem. Ges. **21**, 509.

general application, and for many cases it is better than any of the other methods in common use.

The crude chloride of the new base was decomposed with a strong solution of sodium hydroxide, the amine was taken up with ether, the ethereal solution was dried with stick potash and then with metallic sodium, and was submitted to fractional distillation.

Diethyl-carbinamine, $\frac{C_2H_5}{C_2H_5}$>$CHNH_2$, boils at 89°–91°. It is a colorless, mobile liquid with a penetrating, ammoniacal odor. It absorbs carbon dioxide greedily from the air, and a few drops left for some time in a loosely-stoppered test-tube were converted into well-formed, needle-shaped crystals. These are permanent in the air. The base is miscible with water in all proportions. Considerable heat is evolved when it is mixed with a small amount of water.

The specific gravity of the base is $D\frac{20°}{4°} = 0.7487$.

I. 0.1496 gram of the base gave 0.3796 gram CO_2 and 0.2042 gram H_2O.

II. 0.1433 gram of the base gave 0.3625 gram CO_2 and 0.1987 gram H_2O.

	Calculated for $\frac{C_2H_5}{C_2H_5}$>$CHNH_2$.	Found. I.	II.
C	68.97	69.20	68.97
H	14.94	15.17	15.41

The *chloride*, $C_5H_{11}NH_2.HCl$, is very easily soluble in water and in alcohol. It crystallizes from a concentrated aqueous solution in needles which are not deliquescent and which melt at 216°–217°.

0.0965 gram of the salt dried at 135° gave 0.1111 gram AgCl.

	Calculated for $C_5H_{11}NH_2.HCl$.	Found.
Cl	28.75	28.48

The *chloroplatinate* crystallizes in needles which are very easily soluble in water and in alcohol.

The *nitrite* can be prepared by passing nitrous anhydride into a solution of the base in dry ether. The salt separates in the form of white needles. If the ether is moist, a concentrated solution of the nitrite separates. The crystallized salt can be readily obtained by evaporating the aqueous solution over sulphuric acid *in vacuo*.

The salt is extremely deliquescent. At ordinary temperatures both the dry salt and its concentrated solution appear to be entirely stable. The dilute solution (1 : 2000) can be heated to boiling for some time without appreciable decomposition, as was shown by quantitative color reactions with meta-phenylene-diamine. Evaporation to dryness causes an almost complete decomposition of the salt.

Dipropyl-carbinamine (*4-amino-heptane*).

Dipropyl-ketone was prepared by distilling normal calcium butyrate. The ketone was converted into the oxim and amine by methods similar to those used for diethyl-ketone. Dipropyl-carbinamine, $\begin{matrix}CH_3CH_2CH_2\\CH_3CH_2CH_2\end{matrix}>CHNH_2$, is a colorless, mobile liquid with an ammoniacal odor. It is but very slightly soluble in water. It boils at 139°–140°. The base absorbs carbon dioxide rapidly from the air, forming a carbonate which crystallizes in needles and which is very difficultly soluble in water. It dissolves more easily than the free base, however, as its solution becomes turbid on the addition of sodium hydroxide.

The specific gravity of the base is $D\frac{20°}{4°}=0.7667$.

0.1901 gram of the base gave 0.5033 gram CO_2 and 0.2520 gram H_2O.

	Calculated for $\begin{matrix}C_3H_7\\C_3H_7\end{matrix}>CHNH_2$.	Found.
C	73.04	72.20
H	14.78	14.73

The *chloride*, $C_7H_{15}NH_2.HCl$, is easily soluble in water and alcohol. It melts at 241°–242°. It crystallizes in needles.

0.1090 gram of the chloride gave 0.1036 gram AgCl.

	Calculated for $C_7H_{15}NH_2.HCl$.	Found.
Cl	23.43	23.49

The *chloroplatinate* separates in light yellow-colored scales which are difficultly soluble in water, more easily soluble in alcohol.

The *nitrite* is very easily soluble in water. When a little more than the calculated amount of a strong solution of sodium nitrite is added to the chloride nothing separates and no decomposition takes

place in the cold solution. When the solution is heated in boiling water for three-fourths of an hour, about 80 per cent. of the theoretical amount of nitrogen is evolved. It is noticeable that in this and in other similar cases the decomposition takes place rapidly in a concentrated solution, while it is much slower in a dilute solution, and with a certain degree of dilution appears to cease altogether. Kastle has observed a similar conduct on the part of silver chloracetate.[1] In the light of the theory of electrolytic dissociation it seems probable that the molecules which have become dissociated by dilution will no longer decompose in the ordinary manner.[2] It has recently been shown[3] that even ammonium nitrite becomes comparatively stable in dilute solutions, apparently for the same reason.

Di-isobutyl-carbinamine (2-6-*dimethyl*-4-*amino-heptane*).

Valerone was prepared from isovaleryl chloride (b. p. 115°–117.5°) by treatment with anhydrous ferric chloride by the method of Hamonet.[4] The yield was very poor. From 84 grams of valeryl chloride only 4 grams of valerone, boiling at 168°–172°, were obtained. Schmidt[5] gives the boiling-point of valerone as 181°–182°. Hamonet,[6] however, found the boiling-point 165°–167°, but thinks that his preparation was not pure. Schmidt prepared his valerone by distilling calcium valerianate, and obtained a yield of only 10 per cent. of the crude distillate. While the yield by Hamonet's method is no better, a consideration of the boiling-points of related compounds makes it probable that the valerone prepared by Schmidt was the normal compound (5-nonanone), while that obtained by Hamonet and myself was the isovalerone (2-6-dimethyl-4-heptanone). The boiling-point of the base given below, as the latter was prepared from a crystallized chloride, is probably more trustworthy than that of the valerone. That boiling-point indicates that the true boiling-point of isovalerone must be about 170°, since with increasing molecular weight the boiling-point of the amine approaches that of the corresponding ketone.

The valerone (4 grams) was converted into the oxim by heating on the water-bath for two hours with hydroxylamine chloride (4

[1] This Journal **14**, 586.
[2] See Ostwald: Zeit. f. phys. Ch. **11**, 431.
[3] Anzeli and Boeris: Gazz. Chim. **22**, 2, 349.
[4] Ber. d. chem. Ges. **22**, R. 766.
[5] *Ibid.* **5**, 600.
[6] Bull. Soc. Chim. (3) **2**, 334–347.

grams), caustic soda (2 grams), water (12 cc.) and alcohol (10 cc.). The oxim was taken up with ether, the solution washed twice with water to free it from alcohol, dried with calcium chloride, and the ether distilled off. The oxim remaining was reduced as usual. The chloride of the base obtained was crystallized from water, and the base separated from the chloride was dried with stick potash and metallic sodium.

Di-isobutyl-carbinamine is a colorless liquid with a strong ammoniacal odor. It boils at 166°–167°. It is almost insoluble in water, and caustic soda produces a turbidity even in very dilute solutions of the chloride. The specific gravity is $D\frac{20°}{4°}=0.772$.

I. 0.1394 gram of the base gave 0.3808 gram CO_2 and 0.1830 gram H_2O.

II. 0.2251 gram of the base gave 0.6171 gram CO_2 and 0.2950 gram H_2O.

	Calculated for $(CH_3)_2.CH.CH_2$ / $(CH_3)_2.CH.CH_2$ >$CHNH_2$.	Found. I.	Found. II.
C	75.52	74.51	74.77
H	14.69	14.58	14.57

The chloride, $C_9H_{19}NH_2.HCl$, crystallizes in needles which are moderately soluble in water. These melt at 247°–248° without apparent decomposition.

0.1107 gram of the chloride gave 0.0886 gram AgCl.

	Calculated for $C_9H_{19}NH_2HCl$.	Found.
Cl	19.78	19.79

The *chloroplatinate* consists of fine needles of a light yellow color. These are almost insoluble in water.

The *carbonate* forms rapidly in white needles when the base is exposed to the air. These are almost insoluble in water, easily soluble in alcohol.

The *nitrite* is precipitated in the form of white, fine needles, easily soluble in water when a strong solution of sodium nitrite is added to a strong solution of the chloride. About 79 per cent. of the theoretical amount of nitrogen was evolved when the chloride was heated for a short time on the water-bath with a little more than the calculated amount of sodium nitrite.

When nitrous anhydride is passed into an ethereal solution of

the base a crystalline salt is precipitated. When a solution of the salt obtained in this way is evaporated on the water-bath a crystalline residue remains, which gives qualitative tests for nitrous acid. A quantitative examination, however, shows that the nitrite has been largely decomposed. As an exactly similar test was relied on to establish the stability of the nitrite of hexamethylene-diamine,[1] it was thought best to test the conduct of that body once more.

Hexamethylene-diamine (1-4-*diamino-cyclo-hexane*).

A small portion of a chloride of the base remaining from a previous preparation[2] was recrystallized from water and washed with strong alcohol, in which it is very difficultly soluble. An analysis of the purified chloride gave 37.49 per cent. of chlorine. Theory requires 37.97 per cent. When this chloride was heated on the water-bath for half an hour with a little more than the calculated amount of sodium nitrite, about 23 per cent. of the theoretical amount of nitrogen was evolved, or a little less than one atom of nitrogen for one molecule of the base. While it is certain that some decomposition takes place, it does not appear to occur in the normal manner. I hope to make a further study of the matter, and especially of the products of decomposition.

Dihydro-meso-anthramine.

Meso-anthramine was prepared from anthranol by heating it in sealed tubes with strong aqua ammonia.[3] It was reduced to the dihydro compound by means of alcohol and sodium. There was some evolution of ammonia during the reduction, showing the strong tendency of the base to be converted into anthracene by the loss of ammonia.[4]

The chloride of the base when treated with a strong solution of sodium nitrite in the cold suffers no decomposition, but on boiling for a short time about 79 per cent. of the theoretical amount of nitrogen is evolved. The main product of the decomposition is anthracene.

Diphenyl-carbinamine (*Benzhydrylamine*).[5]

The amine was prepared by the reduction of the oxim by means of alcohol and sodium. This method seems better than the one

[1] Baeyer and Noyes: Ber. d. chem. Ges. **23**, 2172. [2] *Loc. cit.*
[3] Goldmann: Ber. d. chem. Ges. **23**, 2522. [4] *Ibid.* **23**, 2526.
[5] I am indebted to Mr. E. Brown for the preparation of this amine.

used by Goldschmidt.[1] When a strong solution of sodium nitrite is added to a solution of the chloride of the base the nitrite separates in well-formed needles which are somewhat difficultly soluble in water. A quantitative colorimetric determination of nitrous acid in these needles showed that they consisted of the pure nitrite. Both the needles and their aqueous solution appear to be perfectly stable at ordinary temperatures. When the concentrated solution of the nitrite is heated in the water-bath for half an hour about 83 per cent. of the theoretical amount of nitrogen is evolved. Diphenyl-carbinol appears to be the main product of the decomposition.

July, 1893.

NOTES ON THE OXIDES CONTAINED IN CERITE, SAMARSKITE, GADOLINITE, AND FERGUSONITE.

By Wolcott Gibbs, M. D.,
Rumford Professor (Emeritus) in Harvard University.

In the present paper I have brought forward a number of observations and analyses which I hope will be of service to those who are engaged in the study of the rarer earths. The subject is one of such extreme difficulty, that even the results of an imperfect study may have value.

For the material which I have employed I have been chiefly indebted to Dr. Waldron Shapleigh, Chemist to the Welsbach Incandescent Light Company, by whom I have been liberally supplied with various preparations in a state of considerable purity. I have also to make my acknowledgments to Professor Everhart, from whom I have received a considerable quantity of gadolinite from the well known locality in Llano County, Texas. The material given me by Dr. Shapleigh consisted in part of beautiful crystalline double nitrates of the earths and ammonium, and in part of crude oxides. The double nitrates contained only the earths present in cerite, and for the most part only Ce_2O_3, Ln_2O_3, Ps_2O_3, and Nd_2O_3, with very small relative quantities of

[1] Ber. d. chem. Ges. **19**, 3233.

Y_2O_3, and traces only of other earths. In converting the crude oxides into sulphates it is best to sift the fine powder slowly upon the surface of cold dilute sulphuric acid. The sulphates are then formed at once as fine crystalline powders free from hard lumps. Another method sometimes applicable with advantage consists in mixing the oxides with an excess of ammonic sulphate, and then igniting slowly in porcelain crucibles, which are to be heated in a muffle to low redness until vapors are no longer given off. The sulphates then present a beautiful snow-white soft crystalline powder, and readily form saturated solutions with cold water. In all work with the rare earths, oxalates from their insolubility play a very important part. They may, as all chemists know, be readily converted into sulphates by treatment with sulphuric acid and careful expulsion of the excess of this last by heat. I have found it more convenient to mix the oxalate intimately with an excess of ammonic sulphate and heat carefully in a muffle, as in the last case. The resulting sulphates are perfectly soluble without packing together if sifted upon the surface of cold water. They are also perfectly neutral. The oxalates may also be converted into chlorides by mixing them intimately with ammonic chloride and igniting the mixture in a muffle very gently.

Determinations of mean atomic mass are now always employed in the study of the mixtures of oxides which present themselves in the attempt to effect separations. Very accurate results are obtained by the usual method of converting a weighed quantity of oxides into the equivalent weight of sulphates by treatment with sulphuric acid and subsequent careful ignition. Probably this could be done more conveniently, and in less time, by igniting the oxides in porcelain crucibles in a muffle, after mixing carefully with ammonic sulphate, but upon this point I have made no quantitative experiments.

In all my work I have employed the analysis of the oxalates as convenient and accurate. It is, however, necessary to insist upon several points of detail. In the first place I remark that the preparation of perfectly homogeneous mixtures of the oxalates requires much care. It is best to precipitate by a hot dilute solution of oxalic acid added slowly in small but distinct excess to a hot dilute solution of the mixed chlorides or nitrates. The precipitated oxalates are then to be thoroughly washed by decantation with hot distilled water. This requires in general a large quantity of water, and must be continued until the washings contain no trace

of oxalic acid and give no cloudiness with ammonia. Auer von Welsbach's process, which consists in adding a very dilute solution of the nitrates (or chlorides) to a hot dilute solution of oxalic acid, gives the oxalates in a state of very fine subdivision and perfectly free from hard masses. The mixed washings on saturation with ammonia sometimes give a precipitate of oxalates, though in small quantity. These oxalates may be washed and mixed with the main portion. The mass is to be dried upon a water-bath, and then thoroughly mixed in a dry mortar. Only in this manner is it possible to obtain a mass of oxalates sufficiently homogeneous to yield corresponding results when different portions are analyzed. The determination of the mean atomic mass in the oxalates prepared as above involves only the determination of the percentages of oxide R_2O_3 and of C_2O_3, the water present being of course without influence. Here I may remark that, as has doubtless been observed by other chemists, the last portions of water require a very high temperature for expulsion. The details of the method which I employ are as follows: From 0.5 gram to 1 gram of the oxalate is to be gently heated until the greater part of the water and carbonic dioxide have been driven off, and then at a full red heat for fifteen to twenty minutes with a blast lamp to a constant weight. During ignition the crucible is best placed at an angle, and partly uncovered to permit free access of air. The mixed oxides do not retain a weighable amount of carbonic dioxide. To determine C_2O_3, from 0.3 gram to 0.4 gram of the oxalate are to be weighed into a 250-cc. flask; 20 cc. of water and 30 cc. of dilute sulphuric acid, 1 : 6 by volume, are then to be added and the flask is to be gently heated upon a sand-bath until the solution is complete, when the hot liquid is to be titrated with carefully standardized permanganate. The following analyses will show the correspondence between the results obtained by the above described method and those obtained by the sulphate process. In an oxalate from a perfectly colorless nitrate of lanthanum and ammonium sent me by Dr. Shapleigh,—

(1) 0.3344 gram gave 0.1009 gram C_2O_3 = 30.15 per cent.
(2) 0.3274 gram gave 0.09895 gram C_2O_3 = 30.07
(3) 0.3726 gram gave 0.1120 gram C_2O_3 = 30.08
(4) 0.3485 gram gave 0.1050 gram C_2O_3 = 30.11
(5) 0.5931 gram gave 0.2706 gram R_2O_3 = 45.61
(6) 0.5977 gram gave 0.2728 gram R_2O_3 = 45.64

The means are 30.10 per cent. C_2O_3, and 45.625 per cent. R_2O_3. The mean atomic mass calculated from the above is 139.70. Dr. Shapleigh found by the sulphate method 139.75, 139.72, 139.67, mean 139.71.

The necessity of thoroughly mixing the oxalates will appear from the following analyses made with oxalates simply washed and dried:

(7) 0.3549 gram gave 0.1274 gram $C_2O_3 = 35.88$ per cent.
(8) 0.3697 gram gave 0.1316 gram $C_2O_3 = 35.59$
(9) 0.3807 gram gave 0.1382 gram $C_2O_3 = 36.29$
(10) 0.6550 gram gave 0.2869 gram $R_2O_3 = 43.79$
(11) 0.6125 gram gave 0.2699 gram $R_2O_3 = 44.07$

The same oxalates carefully mixed in a mortar were also analyzed for comparison:

(12) 0.3357 gram gave 0.1213 gram $C_2O_3 = 36.16$ per cent.
(13) 0.3856 gram gave 0.1393 gram $C_2O_3 = 36.13$
(14) 0.6538 gram gave 0.2906 gram $R_2O_3 = 44.45$
(15) 0.7074 gram gave 0.3145 gram $R_2O_3 = 44.46$

The analyses leave no doubt whatever as to the necessity of carefully mixing the precipitated oxalates. They also show that in determinations of atomic mass by the sulphate method both oxalates and oxides should be well ground up to secure homogeneity. It has been shown that the oxalate and sulphate methods executed with proper care give equally accurate results. Each has its advantages, and in this respect there is but little choice. As the study of the rarer earths as now conducted usually depends more or less upon the properties of the double salts which they form with potassic and sodic sulphates, it may be well to call attention to facts not, I believe, noticed in printed papers, though doubtless recognized. The first is that the earths in the double sulphates may be converted directly into oxalates by boiling the sulphates with chlorhydric and oxalic acids, and then diluting with much water. The second fact is that oxalates obtained in this way, as from any alkaline solutions, should always be converted into oxides by ignition. These should then be dissolved in chlorhydric acid, again precipitated by oxalic acid, and the oxalates thoroughly washed.

In determining atomic masses by either the sulphate or oxalate method, the assumption is tacitly made that all the oxides taken

for analysis are of the type R_2O_3. This is not true when cerium is present, as in that case a portion at least of this metal is present as CeO_2 after ignition. Higher oxides than R_2O_3 are also present to some extent, at least when praseodymia and neodymia are mixed with ceria, or even when this last oxide is absent. Ceric oxide is not reduced by a full red heat to cerous oxide, or even by a current of hydrogen, at least in a crucible. The error committed is not, however, large when we consider the cerium as Ce_2O_3 instead of Ce_2O_4, and is still less in the cases of the other oxides. When great accuracy is necessary, it may be well to remove the four cerite oxides by means of potassic or sodic sulphate before determining the atomic mass.

In a number of analyses I determined the percentage of oxides by simply igniting the oxalate with a weighed quantity of pure sodic tungstate. This method gives very accurate results, but, as pure sodic tungstate must always be specially prepared in the laboratory, is not to be greatly recommended. Ceric oxide is not reduced to cerous oxide by heating with the tungstate to a red heat for some time. I may here state that a test for ceria more delicate than that which I gave many years since (PbO_2 and NO_3H) is obtained by employing the oxide of bismuth, Bi_2O_4, in place of plumbic oxide.

With these preliminaries I proceed to special methods of separating the mixed oxides. A series of experiments was first made to determine to what extent differentiation is effected by successive partial precipitations by oxalic acid. The method is of course not new, but, so far as I know, it has not been tested by quantitative analyses, and no attempt has been made to determine the rate of change. The material used in this case was a mixture of sulphates, the sulphate of neodymium being present in largest quantity. Thoric and other oxides in less quantity were also present. The material was obtained from Dr. Shapleigh in the form of oxides. After careful purification the atomic mass of the oxides was first determined:

(16) 0.5622 gram gave 0.1715 gram C_2O_3 = 30.50 per cent.
(17) 0.4782 gram gave 0.1458 gram C_2O_3 = 30.50
(18) 0.4355 gram gave 0.1326 gram C_2O_3 = 30.47
(19) 0.6100 gram gave 0.2778 gram R_2O_3 = 45.55
(20) 0.6904 gram gave 0.3141 gram R_2O_3 = 45.50

The analyses give as the atomic mass 137.25. A portion of the oxides was then converted into sulphates, and the number of cubic centimeters of a solution of oxalic acid required for complete precipitation determined by experiment with a sufficiently close approximation. A solution of the sulphates having a very fine rose-red color was then precipitated in five successive additions of equal volumes of a solution of oxalic acid. After each addition of the acid the resulting oxalate was filtered off and washed. The washings were then added to the filtrate. It will be seen that in this way the bulk of the solution increased before each precipitation after the first. The results are as follows:

I. (21) 0.3126 gram gave 0.0941 gram C_2O_3 = 30.52 per cent.
(22) 0.3410 gram gave 0.1042 gram C_2O_3 = 30.54
(23) 0.5773 gram gave 0.2820 gram R_2O_3 = 48.84
(24) 0.5856 gram gave 0.2855 gram R_2O_3 = 48.75
Atomic mass 148.60.

II. (25) 0.3563 gram gave 0.1114 gram C_2O_3 = 31.26
(26) 0.3500 gram gave 0.1091 gram C_2O_3 = 31.20
(27) 0.6848 gram gave 0 3317 gram R_2O_3 = 48.43
(28) 0.6664 gram gave 0.3223 gram R_2O_3 = 48.37
Atomic mass 143.35.

III. (29) 0.3500 gram gave 0.1113 gram C_2O_3 = 31.78
(30) 0.3127 gram gave 0.09936 gram C_2O_3 = 31.77
(31) 0.6859 gram gave 0.3345 gram R_2O_3 = 48.75
(32) 0.7087 gram gave 0.3447 gram R_2O_3 = 48.65
Atomic mass 141.55.

IV. (33) 0.3350 gram gave 0.1042 gram C_2O_3 = 31.12
(34) 0.3410 gram gave 0.1060 gram C_2O_3 = 31.09
(35) 0.6369 gram gave 0.2958 gram R_2O_3 = 46.44
(36) 0.6468 gram gave 0.3004 gram R_2O_3 = 46.45
Atomic mass 137.25.

V. (37) 0.2042 gram gave 0.06864 gram C_2O_3 = 33.62
(38) 0.2031 gram gave 0.06828 gram C_2O_3 = 33.62
(39) 0.3045 gram gave 0.1409 gram R_2O_3 = 46.26
(40) 0.3400 gram gave 0.1569 gram R_2O_3 = 46.14
Atomic mass 124.40.

The filtrate from the last portion of oxalates contained only traces of earths. The analyses show that the earths with the high-

est atomic masses are precipitated first by oxalic acid. The average rate of decrease of mean atomic mass is five units for each operation, but the rate is by no means uniform. The results prove that precipitated oxalates must be very carefully mixed mechanically before analysis when more than one earth is present. The analyses also show that four-fifths of the earths might have been precipitated at once by oxalic acid if the object had been to obtain yttria with the least outlay of time and labor, the atomic mass of the last fifth being 124.40.

Oxychlorides.—When the chlorides of the metals belonging to the cerium and yttrium groups, or more generally stated, of the metals yielding the rarer earths, are carefully heated, oxychlorides are formed in greater or less proportion mixed with undecomposed chlorides. We may distinguish these as acid and basic chlorides. Water dissolves out the former very readily and leaves nearly or quite colorless basic chlorides, which are, relatively at least, insoluble. I find that in this way the earths present are separated into two groups, and that by repeating the operation upon each group a second differentiation is effected in each case. The process appears to deserve attention, and to compare very favorably with separation by means of basic nitrates. The details of this method are as follows:

The mixed oxides in as pure a state as possible are to be dissolved in a small excess of pure chlorhydric acid; the solution is then to be evaporated at first on a water-bath, and then on a sand-bath, until a thick syrup is obtained. This is to be transferred to a porcelain crucible, which is then to be heated gently in a muffle. The heat should not be allowed to exceed low redness. Much chlorhydric acid is given off during the heating, and a white mass remains which consists in part of a mixture of oxychlorides, and in part of unaltered chlorides. The mass is then to be treated with hot water in rather small portions at a time, the solution being poured off before each new addition. When the washing is nearly complete, the solution becomes turbid. The white insoluble mass and supernatant liquid are then to be evaporated to dryness, or to a thick syrup, after the addition of enough chlorhydric acid to effect complete solution. The liquid poured off and containing the soluble chlorides is also to be evaporated to dryness, but without addition of chlorhydric acid. We have then two separate portions, of which one, A, contains the soluble

or relatively acid chlorides, and the other, B, the neutralized oxychlorides. Each of these portions is to be treated in the muffle, as in the first case. In this manner two new basic chlorides, B_2 and B_3, and two new acid chlorides, A_2 and A_3, are obtained. The same processes are to be repeated as long as the material lasts. The atomic mass of the oxides taken must first be determined, and afterward the atomic masses of the portions A_1, A_2, A_3, etc., and B_1, B_2, B_3, etc. This enables us to determine the rate of change in the atomic masses produced by the successive operations. Of course, it is only necessary to take a small portion of each product A_1, B_1, etc., for the determination of the atomic mass. The whole process will perhaps be rendered more clear by means of a diagram, and in illustration I shall select the results of actual work in a particular case. The starting-point in this case was a mixture of oxides from Texas gadolinite having the atomic mass 107.5. The data are as follows:

(41) 0.3577 gram gave 0.1357 gram C_2O_3 = 37.94 per cent.
(42) 0.3246 gram gave 0.1228 gram C_2O_3 = 37.81
(43) 0.3999 gram gave 0.1515 gram C_2O_3 = 37.86
(44) 0.6113 gram gave 0.2814 gram R_2O_3 = 46.04
(45) 0.6670 gram gave 0.3064 gram R_2O_3 = 45.94
(46) 0.6303 gram gave 0.2892 gram R_2O_3 = 45.88

Atomic mass 107.5.

B_1 Left. Atomic mass 110.8.

(47) 0.6836 gram gave 0.3289 gram R_2O_3 = 48.11 per cent.
(48) 0.2344 gram gave 0.0904 gram C_2O_3 = 38.57

A_1 Right. Atomic mass 94.75.

(49) 1.2740 grams gave 0.4976 gram R_2O_3 = 39.65 per cent.
(50) 0.2998 gram gave 0.1065 gram C_2O_3 = 35.51

B_2 Left. Atomic mass 117.4.

(51) 0.4327 gram gave 0.2157 gram R_2O_3 = 49.84 per cent.
(52) 0.2860 gram gave 0.1089 gram C_2O_3 = 38.07

A_2 Left. Atomic mass 98.35.

(53) 0.7897 gram gave 0.3714 gram R_2O_3 = 47.03 per cent.
(54) 0.3772 gram gave 0.1566 gram C_2O_3 = 41.52

B_3 Left. Atomic mass 122.

(55) 0.5910 gram gave 0.2803 gram R_2O_3 = 47.43 per cent.
(56) 0.2023 gram gave 0.0710 gram C_2O_3 = 35.09

A_3 Left. Atomic mass 102.8.

(57) 0.4472 gram gave 0.2137 gram $R_2O_3 = 47.78$ per cent.
(58) 0.3067 gram gave 0.1248 gram $C_2O_3 = 40.70$

A_1 Right. Atomic mass 94.75.

(59) 1.2740 grams gave 0.4976 gram $R_2O_3 = 39.05$ per cent.
(60) 0.2998 gram gave 0.1065 gram $C_2O_3 = 35.51$

A_2 Right. Atomic mass 91.65.

(61) 1.0032 grams gave 0.3948 gram $R_2O_3 = 39.37$ per cent.
(62) 0.5057 gram gave 0.1856 gram $C_2O_3 = 36.77$

B_2 Right. Atomic mass 98.6.

(63) 0.7353 gram gave 0.3291 gram $R_2O_3 = 44.75$ per cent.
(64) 0.3343 gram gave 0.1318 gram $C_2O_3 = 39.43$

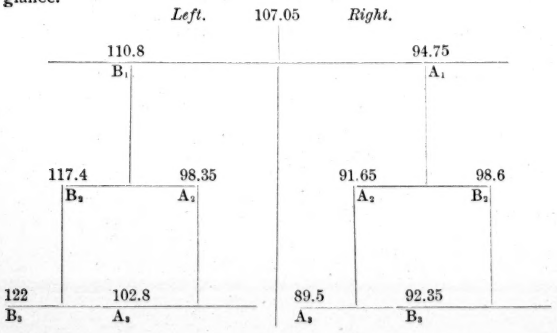
A_3 Right. Atomic mass 89.5.

(65) 0.4864 gram gave 0.2146 gram $R_2O_3 = 44.12$ per cent.
(66) 0.2212 gram gave 0.0929 gram $C_2O_3 = 42.00$

B_3 Right. Atomic mass 92.35.

(67) 0.5183 gram gave 0.2238 gram $R_2O_3 = 43.17$ per cent.
(68) 0.2080 gram gave 0.0834 gram $C_2O_3 = 40.07$

The following diagram enables us to take in all the results at a glance.



It must be noted that in the above and on the diagram, B_1, B_2, B_3, etc., denote basic or oxychlorides; A_1, A_2, A_3, etc., neutral or relatively acid chlorides. The analyses were not pursued further

because the material taken was exhausted by the separations accomplished. The examination of the results obtained in this particular case by the basic-chloride process leads to interesting conclusions. In the first place, it will be remarked that the atomic masses of the insoluble basic chlorides increase with each successive separation into basic and acid chlorides, while the neutral or relatively acid chlorides give diminishing atomic masses. In the cases of these last, three successive operations give a nearly pure yttria, with atomic mass 89.5. The rate of increase of the atomic masses of the successive portions B_1, B_2, B_3, is about 5.3 units for each operation. The rate of decrease of the portions A_1, A_2, A_3, is about 2.6 units for each operation. It is not to be expected that perfectly uniform results will be obtained even when the process is applied to the same mixture of oxides, because the amount of separation into basic and acid chlorides by each operation must depend very much upon the temperature of the muffle and the length of time during which the heat is applied. In the second place, it must be noted that, while a very nearly pure yttria is obtained in three operations, this does not represent the whole quantity of the earth in the compound. It will also be seen that a decided advantage must be secured by making mixtures of the products having nearly the same atomic masses, and then applying the method of separation to these.

Other applications of the method give, as I will now show, substantially similar results: The next substance examined was a mixture of oxides received from Dr. Shapleigh, and obtained from residual mother-liquors of cerite and monazite salts. The oxide was dissolved in chlorhydric acid, and purified by a current of sulphydric acid. Of the mixed oxalates,—

(69) 0.5622 gram gave 0.1715 gram C_2O_3 = 30.50 per cent.
(70) 0.4782 gram gave 0.1458 gram C_2O_3 = 30.50
(71) 0.4355 gram gave 0.1326 gram C_2O_3 = 30.47
(72) 0.6100 gram gave 0.2778 gram R_2O_3 = 45.55
(73) 0.6904 gram gave 0.3141 gram R_2O_3 = 45.50

Atomic mass 137.25.

I also determined the mean atomic mass after separating the cerite earths by means of sodic sulphate in the usual manner. Of course some yttria went down with the double sulphates.

(74) 0.2440 gram gave 0.0946 gram C_2O_3 = 38.77 per cent.
(75) 0.2438 gram gave 0.0946 gram C_2O_3 = 38.80
(76) 0.4597 gram gave 0.2146 gram R_2O_3 = 46.68
(77) 0.3570 gram gave 0.1668 gram R_2O_3 = 46.72
Atomic mass 106.05.

The oxides with atomic mass 106.05 were then treated by the oxychloride process.

Portion B_1 Left.
(78) 0.4027 gram gave 0.1505 gram C_2O_3 = 37.38 per cent.
(79) 0.5204 gram gave 0.1943 gram C_2O_3 = 37.35
(80) 0.6947 gram gave 0.3250 gram R_2O_3 = 46.78
(81) 0.9233 gram gave 0.4323 gram R_2O_3 = 46.82
Atomic mass 111.3.

Portion B_2 Left.
(82) 0.4127 gram gave 0.1464 gram C_2O_3 = 35.49 per cent.
(83) 0.3215 gram gave 0.1142 gram C_2O_3 = 35.51
(84) 0.5885 gram gave 0.2668 gram R_2O_3 = 45.33
(85) 0.6205 gram gave 0.2814 gram R_2O_3 = 45.35
Atomic mass 113.95.

Portion A_1 Right.
(86) 0.4332 gram gave 0.1630 gram C_2O_3 = 37.63 per cent.
(87) 0.3239 gram gave 0.1217 gram C_2O_3 = 37.57
(88) 0.6813 gram gave 0.3062 gram R_2O_3 = 44.94
(89) 0.6749 gram gave 0.3035 gram R_2O_3 = 44.95
Atomic mass 105.1.

Portion A_2 Right.
(90) 0.3317 gram gave 0.1161 gram C_2O_3 = 35.02 per cent.
(91) 0.3216 gram gave 0.1126 gram C_2O_3 = 35.00
(92) 0.6800 gram gave 0.2823 gram R_2O_3 = 41.52
(93) 0.6529 gram gave 0.2709 gram R_2O_3 = 41.50
Atomic mass 104.05.

B_2 Right.
(94) 0.3785 gram gave 0.1314 gram C_2O_3 = 34.73 per cent.
(95) 0.2882 gram gave 0.0999 gram C_2O_3 = 34.68
(96) 0.6187 gram gave 0.2676 gram R_2O_3 = 43.25
(97) 0.6421 gram gave 0.2770 gram R_2O_3 = 43.24
Atomic mass 110.45.

A_3 Left.

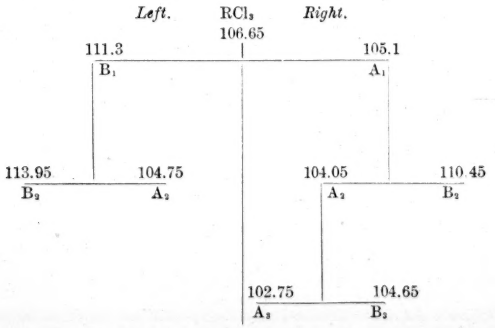
(98) 0.3458 gram gave 0.1290 gram C_2O_3 = 37.31 per cent.
(99) 0.4089 gram gave 0.1523 gram C_2O_3 = 37.24
(100) 0.6892 gram gave 0.3062 gram R_2O_3 = 44.43
(101) 0.5986 gram gave 0.2660 gram R_2O_3 = 44.44
Atomic mass 104.75.

A_3 Right.

(102) 0.3002 gram gave 0.1162 gram C_2O_3 = 38.73 per cent.
(103) 0.3251 gram gave 0.1260 gram C_2O_3 = 38.77
(104) 0.6667 gram gave 0.3031 gram R_2O_3 = 45.44
(105) 0.7642 gram gave 0.3478 gram R_2O_3 = 45.51
Atomic mass 102.75.

(106) B_3 Right.
(107) 0.3426 gram gave 0.1307 gram C_2O_3 = 38.16 per cent.
(108) 0.3401 gram gave 0.1298 gram C_2O_3 = 38.18
(109) 0.8197 gram gave 0.3728 gram R_2O_3 = 45.46
(110) 0.7623 gram gave 0.3467 gram R_2O_3 = 45.47
Atomic mass 104.65.

These determinations exhausted the material employed. The following diagram brings together all the results.



The diagram in the case of the oxides from cerite and monazite shows very clearly that, as with the oxides from gadolinite, the atomic masses B_1, B_2, B_3 increase, while those of A_1, A_2, A_3 diminish, but at a different rate, perhaps, as already remarked,

because the conditions were not precisely the same. It seems very desirable that similar experiments should be made with the basic-nitrate process, which has been so much used, so as to determine which method gives results that converge most rapidly toward the atomic masses of pure oxides. Only in this manner can the relative values of the two methods be determined. I consider it probable that further experience with the oxychloride process will lead to a very material shortening of the process. I have employed for the most part porcelain crucibles holding about 130 cc., but with larger muffles it would be easy to work up a kilogram of oxides at each operation. Also much is to be expected from a judicious mixture of the different products on the right and left having nearly the same atomic masses. All points fairly considered, I am I believe justified in offering the oxychloride process as worthy of further trial.

It appeared possible that basic bromides might be more advantageous than basic chlorides as means of differentiation, but the experiments made were not conclusive on this point. Observing the formation of beautiful, well defined crystals when the oxides from gadolinite and the cerite and monazite residues were dissolved in chlorhydric or bromhydric acid, and the solutions evaporated to a syrupy consistence, I examined two cases. The perfectly colorless and easily soluble crystals obtained from gadolinite earths free from cerite earths by chlorhydric acid after two successive crystallizations were analyzed.

(111) 0.3248 gram gave 0.1293 gram C_2O_3 = 39.82 per cent.
(112) 0.3000 gram gave 0.1450 gram R_2O_3 = 48.34

The atomic mass is 107.10, so that the crystalline chlorides contained the earths in the same proportion in which they were obtained from gadolinite after separation of the cerite earths.

Precisely the same result was obtained with crystallized bromides prepared by dissolving the crude oxides from the cerite and monazite residues in bromhydric acid and evaporating. The beautiful colorless crystals were not quite free from the mother-liquor. Of these crystals,

(113) 0.3418 gram gave 0.1064 gram C_2O_3 = 31.11 per cent.
(114) 0.4266 gram gave 0.1325 gram C_2O_3 = 31.07
(115) 0.6110 gram gave 0.2879 gram R_2O_3 = 47.13
(116) 0.6896 gram gave 0.3293 gram R_2O_3 = 47.02

The atomic mass is 139.55, which is nearly the same as that obtained from the oxides directly, 137.25.

The mother-liquor from the crystals was also analyzed.

(117) 0.3750 gram gave 0.1171 gram Ce_2O_3 = 31.25 per cent.
(118) 0.3237 gram gave 0.1015 gram Ce_2O_3 = 31.37
(119) 0.6752 gram gave 0.3180 gram R_2O_3 = 47.10
(120) 0.8150 gram gave 0.3837 gram R_2O_3 = 47.08

The atomic mass corresponding is 138.45. From the above it appears that little, if anything, is gained by crystallization of the chlorides and bromides, at least in the cases cited.

The fact that potassic and sodic sulphates which do not give precipitates of double sulphates in cold saturated solutions of certain earths often give crystalline precipitates on boiling, has doubtless been observed. I do not find, however, that such observations have been noted in published papers. The following analyses will serve to show that valuable results may sometimes at least be obtained by this process.

A quantity of oxides from Samarskite, sent me by Dr. Shapleigh, was dissolved in chlorhydric acid, and precipitated cold by an excess of potassic sulphate. After filtering off the double sulphates, sodic sulphate was added and the solution boiled. An abundant white crystalline salt was obtained. After washing with a little boiling water the double salt was dissolved in chlorhydric acid, and oxalic acid added after large dilution. The oxalates were converted into oxides and these redissolved in chlorhydric acid and again precipitated with oxalic acid. The oxalates were then analyzed.

(121) 0.2853 gram gave 0.1217 gram R_2O_3.
(122) 0.3889 gram gave 0.1660 gram R_2O_3.
(123) 0.5558 gram gave 0.2256 gram CeO_2.

Atomic mass 89.55, which does not sensibly differ from the received atomic mass of yttrium. From this it appears that yttria was separated in quantity by one operation after the separation of the cerite oxides.

Application of the coballamines to the separation of the oxides.—Many experiments were made to determine whether the sulphates of organic alkaloids would form double salts with the sulphates of the rare earths which could be made available for separations. These did not lead to satisfactory results, though

double salts were formed in some cases. It then occurred to me that the sulphates and other salts of various cobaltamines, on account of their disposition to form highly crystalline compounds, might be employed with advantage. Following are the results of this investigation.

A solution of sulphate of luteocobalt precipitates completely from their cold solutions as neutral sulphates the four cerite earths now known, namely, the oxides of cerium, lanthanum, praseodymium, and neodymium. The double sulphates are beautifully crystalline, have an orange-red color, and are very slightly soluble in cold water, but, practically at least, insoluble in boiling water. They are soluble in acids, and sometimes crystallize from weak acid-solutions. All these compounds appear to have the same constitution, which is that of the salts discovered many years since by myself, and analyzed in my laboratory by C. H. Wing.[1] I find, however, that the constitution of both the luteo- and roseo-salts may be much more accurately represented by the formulas:

I. $2\{Co_2(NH_3)_{12}(SO_4)_3 + Ce_2(SO_4)_3\} + 3aq.$
II. $2\{Co_2(NH_3)_{12}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 3aq.$
III. $2\{Co_2(NH_3)_{10}(SO_4)_3 + Ce_2(SO_4)_3\} + 9aq.$
IV. $2\{Co_2(NH_3)_{10}(SO_4)_3\} + 3\{Ce(SO_4)_2\} + 9aq.$

Mr. W. J. Karslake has arrived independently at the same formulas, and has calculated the percentages as required by them.

For Formula I.		Calculated.	Found.
$24NH_3$	408	16.93	16.75 (loss)
$4Co$	236	9.79	9.31
$4Ce$	560	23.24	24.10
$12SO_4$	1152	47.80	47.77
$3H_2O$	54	2.24	2.07
	2410	100.00	

For Formula II.		Calculated.	Found.		
$24NH_3$	408	17.97	17.73 (loss)		
$4Co$	236	10.40	10.80	10.74	10.44
$3Ce$	420	18.57	16.90	17.27	17.54
$12SO_4$	1152	50.75	51.80	51.83	52.22
$3H_2O$	54	2.37	2.47	2.21	2.39
	2270	100.00			

[1] Am. J. Sci. [2] **49**, 363.

For Formula III.		Calculated.	Found.
$20NH_3$	340	14.72	14.24 (loss)
$4Co$	236	10.22	10.39 9.60
$3Ce$	420	18.18	18.18 19.36
$12SO_4$	1152	49.86	49.73 49.97
$9H_2O$	162	7.02	7.00 7.31
	2310	100.00	

For Formula IV.		Calculated.	Found.
$20NH_3$	340	13.88	15.13 (loss)
$4Co$	236	9.64	9.90
$4Ce$	560	22.85	20.99
$12SO_4$	1152	47.02	47.23
$9H_2O$	162	6.61	6.75
	2450	100.00	

The analyses are those of Wing. Recent determinations of the molecular masses of the cobaltamines have shown that the chlorides, for example, of roseocobalt and luteocobalt are represented respectively by the formulas $Co(NH_3)_5Cl_3$ and $Co(NH_3)_6Cl_3$. I have kept the old formulas only to permit an easy comparison with those given by Wing, and the matter is not one of consequence in this place. It may also be remarked that, as cerium is at present the only one of the group which forms a well defined oxide higher than R_2O_3, the two formulas II and IV cannot be generalized by substituting the symbols of other elements for that of cerium. I have endeavored, however, to prepare such compounds by adding a solution of $Lc_2(SO_4)_3$ to one containing the sulphates of oxides other than the cerite oxides, and then adding some oxidizing agent, as for instance potassic permanganate, chlorine, or bromine. No decisive results were obtained. It is at least probable that all the earths the sulphates of which in cold solutions give only slightly soluble double sulphates with potassic and sodic sulphates will also give insoluble double sulphates with sulphate of luteocobalt. These earths are, so far as now known, Ce_2O_3, La_2O_3, Nd_2O_3, Ps_2O_3, Sm_2O_3, Sc_2O_3, while the following give soluble double sulphates: Er_2O_3, Y_2O_3, Yb_2O_3, and Tb_2O_3. The four cerite oxides cited are not the only ones which give insoluble crystalline precipitates with sulphate of luteocobalt in the cold, but I am not at present able to give more accurate

information on this point. On the other hand, we meet in the case of luteocobalt sulphate with some of the relations which present themselves when the alkaline sulphates are employed. Thus sulphate of yttria is not precipitated by sulphate of luteocobalt when alone, but when mixed with the sulphates of the cerite group more or less of a double sulphate of luteocobalt and yttria is always thrown down, and the same appears to be true for the sulphates of some other earths. In such cases the mixed sulphates of earths and luteocobalt should be gently heated in a muffle until the cobaltamine is completely decomposed and the excess of sulphuric acid is expelled. The residual sulphates of cobalt and the earths should then be dissolved in cold water, filtered, and again precipitated by sulphate of luteocobalt, allowing the mixture to stand twenty-four hours. The supernatant liquid appears then to contain all but the four cerite earths. This point is, however, not yet sufficiently proved, and I reserve it for further investigation.

The solution from which the double sulphates of the cerite earths and luteocobalt have been separated by decantation or filtration usually gives a more or less abundant crystalline precipitate on boiling. The filtrate from this again gives a precipitate with ammonia. The above stated facts are precisely those which we meet with in employing the alkaline sulphates in place of the sulphate of luteocobalt. I have also employed the sulphatochloride of luteocobalt, $Lc_2(SO_4)_2Cl_2$, as a precipitant, and find that double salts are sometimes formed which are much more insoluble than those obtained with the sulphate, excepting only in the cases of the four cerite earths. These contain chlorine as well as sulphuric oxide, and they are sometimes at least formed when sulphate of luteocobalt is added to a solution containing the chlorides of metals of the cerium and yttrium groups. Sulphate of roseocobalt gives in general the same result as sulphate of luteocobalt, only the salts formed in this case are more soluble in both cold and hot water. Experiments with the sulphates of xanthocobalt and croceocobalt have not yet led to valuable results. Certain sulphates of the earths appear to give with sulphate of luteocobalt only hydroxides of the metals, $R(OH)_3$. In this case it seems more probable that a true double sulphate is at first formed and then decomposed, sulphuric acid being set free.

The following results may be of interest in this connection. A portion of earths from Fergusonite sent me by Dr. Shapleigh was converted into sulphates; the cerite earths had been separated by sodic sulphate, and the solution of the earths gave no further precipitate with this. A solution of sulphate of luteocobalt gave no precipitate with this solution in the cold, but on boiling a very abundant crystalline precipitate, insoluble or very slightly soluble in boiling water. The filtrate from these crystals gave only a small precipitate with ammonia, so that the luteocobalt salt must have contained almost all the earths other than the cerite earths. These are known to consist chiefly of yttria. The crystalline precipitate obtained as above by boiling, and insoluble in boiling water, dissolved completely in a large quantity of cold water. The nitrates of roseocobalt and luteocobalt give, in many cases at least, finely crystalline precipitates with the nitrates of the earths. In certain cases, white gelatinous precipitates of hydroxides are formed at the same time, probably as in the case of the sulphates above cited, in consequence of the formation of double nitrates and their subsequent decomposition into free acid and hydroxide. This makes a new mode of differentiation which may prove to be of use, and to which I shall return hereafter. As an instance I may cite the case of the neutral nitrates of the gadolinite earths, from which the cerite earths have been separated by sodic sulphate. A strong solution of these nitrates gives with nitrate of roseocobalt, $Rc(NO_3)_3$, in a short time a bright orange, highly crystalline, and a dirty white, gelatinous precipitate. Both contain earths. The same is true for neutral nitrates from Samarskite, and from the cerite and monazite residues already mentioned. The nitrate of roseocobalt must be in excess. I have already stated that the action of the sulphates of roseocobalt and luteocobalt upon the sulphates of the earths closely resembles that of the alkaline sulphates. The advantage of using the cobaltamines consists, in part, in the fact that the double sulphates of these and the earths are highly crystalline and exceptionally well defined, and that they are in some cases at least very much less soluble than the alkaline double sulphates. The chief disadvantage is that the cobaltamines must be specially prepared for use, and that the most valuable of them—the sulphate of luteocobalt—is not easy to prepare in quantity and in a state of purity. Professor Morris Loeb has, however, found that sulphate of roseocobalt may be converted

into sulphate of luteocobalt by heating with strong ammonia water under pressure, as for instance in sealed tubes; and as the sulphate of roseocobalt is easily prepared, this process is perhaps the best.

A solution of sulphate of luteocobalt gives a very insoluble yellow crystalline precipitate with sulphate of thoria, $Th(SO_4)_2$. It gives also slightly soluble precipitates with uranic sulphate, UO_2SO_4, and with a solution of ferric alum which has undergone dissociation by solution. This last precipitate appears to have the formula $Fe_2O.(SO_4)_2 + Lc_2(SO_4)_3$.

It is my hope to be able to return to the subject in greater detail.

Relations of the oxides to lactic acid.—A portion of the oxides obtained from Samarskite by Dr. Shapleigh after the cerite oxides had been separated by sodic sulphate was boiled with pure lactic acid, and gave an amethyst-red solution. On standing, this solution gave two kinds of crystals, which were very distinct and well defined. These were beautiful red flat prisms, and distinct bright yellow granular crystals. The quantity was too small to permit a more thorough examination, and I did not obtain the same result a second time with other Samarskite oxides. In one experiment, however, the solution of the oxides was deep orange, and after a time deposited crystals with a fine orange color.

The lactates of the cerite earths and of the Samarskite earths which have not been treated with potassic or sodic sulphate give beautiful white feathery crystals, which dissolve with difficulty in hot water.

Relations of mercurous nitrate and mercuric oxide to cerite earths.—A solution of mercurous nitrate gives in general no precipitate with neutral nitrates of the cerite earths. In one experiment, however, in which I employed nitrates from a commercial oxalate, added a solution of mercurous nitrate, and then boiled with free mercuric oxide, the color of the oxide changed to a grayish tint. After filtering and washing, the filtrate was found to contain abundance of didymium (Nd and Ps). The precipitate after washing with boiling water was heated to redness in a platinum crucible, when a clear yellow powder remained. This dissolved in dilute nitric acid to a colorless liquid, which gave no didymium bands with the spectroscope. On adding water to the nitric acid solution a beautiful bright yellow crystalline powder was

thrown down. When the oxides were treated with sulphuric acid a white crystalline mass was formed. Hot water gave with this a fine bright yellow crystalline precipitate. I did not obtain these results with any other samples of cerite oxalates. So far as I am aware no known earths exhibit the reactions with nitric and sulphuric acids above described.

Relations of the Samarskite oxides to acid molybdates, and to phospho-tungstates and phospho-molybdates. — To determine whether any of the oxides contained in Samarskite were capable of forming complex inorganic acids the following experiments were made with a bright yellow mixture of oxides prepared by Lawrence Smith's process with fluohydric acid. The quantity at my disposal was less than five grams, and I am not certain that the cerite oxides had been removed by sodic sulphate.

1. With 10:5 phospho-molybdate of ammonium. The mixed oxides dissolved very easily on boiling with solutions of the phospho-molybdate, giving a fine orange solution. The action of the solution of phospho-molybdate upon the oxides seemed to give instantly a crystalline mass, which on boiling with some excess of phospho-molybdate dissolved. The solution gave beautiful orange-brown crystals, but after twenty-four hours the solution was clear and had a fine rose-color. This solution gave no absorption bands with the spectroscope. With ammonic oxalate it gave a white crystalline precipitate with a clear rose-red solution. This on evaporation to dryness in a platinum vessel gave a rose-red mass, which when heated fused to a greenish mass. The white oxalate settled slowly. The orange crystalline salt dissolved almost completely in boiling water, but some yellow crystalline matter remained. On standing, the solution deposited crystals of a yellow salt.

2. With 14:6 molybdate of ammonium. A solution of 14:6 molybdate of ammonium (commonly written $7MoO_3.3(NH_4)_2O$) also readily dissolved the mixed oxides and gave a deep orange solution. On standing twenty-four hours this gave bright yellow and afterwards very beautiful glittering orange-red crystals. The two kinds of crystals redissolved gave with mercurous nitrate a pale yellow flocky precipitate, which on boiling and standing became bright yellow and highly crystalline. The least soluble crystals were also redissolved separately, and after twenty-four hours crystallized in beautiful prehnitic groups. The orange

mother-liquor from these crystals gave the reaction with mercurous nitrate mentioned above. It seems probable from the above that 14 : 6 molybdate of ammonium gives at least two distinct salts.

3. With 24 : 2 sodic phospho-tungstate. A solution of this salt also dissolved the Samarskite oxides very readily on boiling, giving a fine orange-red solution which soon deposited an abundance of yellow needles. These dissolved readily in hot water to a yellow solution with an orange tint. Yellow needles quickly formed in abundance. After an hour the still slightly warm mother-liquor was poured off and allowed to stand. Two kinds of crystals separated,—very distinct, rather large granular orange crystals in much the larger quantity, and very small granular yellow crystals, differing much from the last in appearance. The two kinds of crystals were dissolved together in hot water, and after a time gave flocky masses of yellow crystals.

I did not succeed in obtaining the same results with other preparations of Samarskite oxides. This will not surprise those who have worked with the rare earths, and who have noticed the difference in the reactions which depends upon difference in the proportions of the mixed oxides. It has, I believe, escaped notice that the same occurs with mixtures of the different metals of the platinum group, as long since shown by Claus.

The compounds with molybdic oxide and with phospho-molybdic and phospho-tungstic acids may prove to be only salts of the earths, and not of complex acids. They appear to deserve further attention as means of separation. As the minerals belonging to the same group with gadolinite resemble each other very closely in their physical characters, it is possible that the yellow oxides above mentioned were not prepared from Samarskite, but from some other mineral.

Analyses 1 to 46 and from 69 to 122 inclusive were made by Mr. Edward L. Smith; from 47 to 68 inclusive by Mr. Wm. J. Karslake. My grateful acknowledgments are due to both.

NEWPORT, R. I., *July* 30, 1893.

Contributions from the Chemical Laboratory of Harvard College.

ON THE OCCLUSION OF GASES BY THE OXIDES OF METALS.[1]

By Theodore William Richards and Elliot Folger Rogers.

In the course of an investigation upon the atomic weight of copper, recently conducted in this Laboratory, it was noted that cupric oxide prepared by the ignition of the nitrate always contains a considerable amount of occluded gas, which is composed mainly of nitrogen.[2] Cupric oxide prepared from the carbonate, on the other hand, appears to possess no such property of occluding gases. Since the material used by Hampe and others had all been made by the former method, it was at once evident that the occluded gas contained in the oxide was wholly responsible for the formerly accepted erroneous results for the atomic weight of copper.

The results of these experiments suggested the possibility that gases might be occluded by all oxides prepared in this way from the nitrates. It became a matter of much importance to test the point, for such oxides have often furnished the starting-point for determinations of atomic weights.

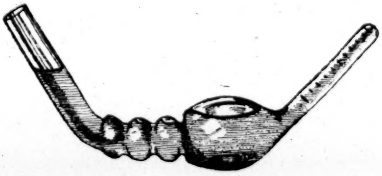
The method adopted in the present research was precisely similar to that used in the case of the cupric oxide. Since it is by no means certain that indefinite heating in a vacuum could drive out all the gas from the compact, often crystalline, compound under examination, the material was dissolved in acids under such conditions that the gas set free could be measured and analyzed.

The simple apparatus needed has been described and explained in the paper already quoted. The material to be investigated was placed in the largest bulb of the bulb-tube shown in the accompanying diagram, and the tube was about half-filled with cold water which had been thoroughly boiled. The whole was then connected with the water-pump, and freed from adhering air bubbles by agitation in the partial vacuum,—the water being allowed to boil gently under the reduced pressure. Subsequently,

[1] Read before the American Academy of Arts and Sciences, May 10, 1893, and reprinted from the Proceedings of that Academy.

[2] Theodore W. Richards: Proc. Am. Acad. Sci. **26**, 281. In 1868 Frankland and Armstrong pointed out this fact; but their statement lacked definiteness, and has since been largely forgotten.

the tube was filled with boiled water and returned to its normal horizontal position. Pure acid was now run in from a pipette, a short piece of glass rod within the large bulb furnishing a means of agitating the oxide during its solution. The gas which was set free was finally collected and measured in the sealed end of the apparatus. In the concluding experiments, where greater accuracy was desired, the gas was transferred, and remeasured in a tube which had been carefully calibrated by means of mercury.



The gas was analyzed with the help of a small Hempel's apparatus made for the purpose. The burette with which the first ten analyses were made was about 7 mm. in internal diameter and could be read to a fiftieth of a cubic centimeter, while that used for the later analyses was only 4 mm. in diameter and could be read with reasonable certainty to the hundredth. The portion of the gas absorbed by caustic potash was assumed to be carbon dioxide, and the further portion which was absorbed by alkaline pyrogallol was assumed in like manner to be oxygen. The residue was perfectly inert, and was undoubtedly nitrogen. One sample of this residue obtained from zincic oxide was mixed with oxygen and subjected to the spark of an induction-coil, without diminution in volume. The apparatus and chemicals were tested from time to time by analyses of air.

In every case, the gas while saturated with aqueous vapor was measured at the ordinary temperature and atmospheric pressure of the room. The variations from the mean values of 22° and 76.0 cm. were not sufficient to need attention in crude work of this kind, when working upon such very small quantities of gas.

Zinc Oxide.

Preliminary experiments with this substance gave results exactly corresponding to those obtained from cupric oxide. If the sub-

stance was prepared by ignition of the nitrate, very considerable amounts of gas were found to be occluded; while material of a similar grade of purity in every other respect, made by heating zincic carbonate, appeared to contain no trace of gas.

The oxide used in the first three experiments was made by treating so-called pure zinc with nitric acid, evaporating to dryness, redissolving the zincic nitrate in water with the addition of a little nitric acid, precipitating a small amount of iron with ammonia in slight excess, evaporating the filtrate, and igniting the residue. This gave a faintly yellow oxide.

For the second series, a nearly neutral solution of fairly pure zincic chloride was precipitated while boiling by a solution of sodic carbonate. Part of the basic carbonate thus formed was ignited directly, the oxide thus produced containing no occluded gas (Experiment 4). The remainder was dissolved in nitric acid, evaporated to dryness, and ignited to the full heat of the blast-lamp in a porcelain crucible. Experiments 5, 6, and 7 are analyses of this yellowish sample.

For the third series a solution of "chemically pure" zincic nitrate was allowed to stand over an excess of zinc for some time. The filtered solution was evaporated until a portion of the nitrate had been converted into the basic salt. The whole was then poured into distilled water, and a solution of normal nitrate was thus obtained after the basic salt had been filtered off. This solution was treated a number of times with zincic hydrate,—which had been precipitated by ammonia and washed until free from the salts of this base,—and allowed to stand. The filtered solution was evaporated to dryness and heated in a porcelain crucible to about 240° C. over a ring burner. Part of this was analyzed at once (Experiment 8), part heated by a Bunsen burner (Experiments 9 and 10), and part ignited at a very high temperature in a Hempel clay furnace with the blast-lamp and bellows (Experiments 11 and 12). Experiment 13 was made with a soft white oxide prepared from the basic nitrate.

Analyses 14 to 27 inclusive were made from oxide obtained as follows: Pure white zincic oxide of commerce was dissolved in nitric acid, and carefully washed zincic carbonate was added to this solution in slight excess. The whole was allowed to stand with occasional shaking for some time, and finally filtered and evaporated rapidly by boiling. This gave a sample of the oxide

which was very nearly white after intense heating in a double porcelain crucible.

In Experiments 22 and 23, pure oxygen was introduced into the flame of the blast-lamp used for igniting the zincic oxide, the bottom of the outer crucible being melted where the flame struck it. The material analyzed in Experiment 22 was taken from the layer nearest to the zincic silicate formed in the bottom of the crucible by fusion of the glaze, and that used in Experiment 23 was taken from the top. The zincic oxide of Experiment 24 was heated to a bright yellow heat in the same way. All the edges of the porcelain were rounded, and the cover and the crucible itself were fused to the heavy iron supports on which they rested. After twelve minutes the iron itself began to burn and the ignition was stopped. The oxide was found to be "sintered together," and was of a grayish color, as if it had been reduced in part. The inference was corroborated by the presence of zincic oxide on the cover of the crucible and on the sides of the stack of the furnace. The zincic oxide used in Experiment 25 was treated in a similar manner, but proved to be still darker in color. It was afterwards ignited for some time in an atmosphere of oxygen, in order that no reduced metal might be left.

The materials used in Experiments 26 and 27 were separate samples heated in a double crucible, with the cover of the inner crucible fitting inside the outer one, instead of covering both. This arrangement rendered less likely the entrance of reducing gases, and allowed freer play of air in the furnace. After the latter had been thoroughly heated by the ordinary blast-lamp, oxygen was slowly turned on through a Y tube, to replace a large part of the air in the flame. This gave an intense white heat, which melted and burned the tip of a file in the fraction of a minute. In Experiment 27 the glaze of the inner crucible was fused, and the platinum which separated the two crucibles was cemented to the outer crucible. The crystalline residue of zincic oxide after this treatment was white with the faintest trace of yellow, but no sign of gray. As the crucible would not stand a higher heat, and as any quantitative determination could scarcely be carried on at a higher temperature, no attempt was made to push the heat further.

The fifth series of determinations was made with the object of discovering whether the trace of silica and alkali dissolved from the glass and porcelain might be responsible for the occlusion of

the gases. First, a sample of the purest zinc that could be obtained was treated with a small amount of pure nitric acid in a porcelain dish, and the solution evaporated to small bulk in the presence of an excess of zinc. Upon dilution the basic nitrate, which contained most of the impurities not deposited upon the zinc, was precipitated and removed by filtration. The solution was then evaporated to dryness and the residue ignited in porcelain. (See Experiments 28 and 29.) Another sample of zinc was dissolved in a similar way in platinum, and the resulting solution of the pure nitrate was divided into several portions. One portion was evaporated in glass and ignited in porcelain, the residue containing somewhat more gas than that which had been treated wholly in porcelain. (See Experiments 30, 31, 32, and 33.) Another part was evaporated and ignited in platinum (Experiment 34). This sample was undoubtedly reduced in part by the diffusion of gases from the flame.[1] Still another portion was ignited for a short time only in platinum, the ignition being completed in porcelain (Experiment 35). A fourth portion was ignited for a short time in an open platinum dish with free access of air (Experiment 36). Finally, the remainder of the solution of pure zincic nitrate was evaporated and ignited in a platinum vessel enclosed within one of porcelain. This specimen was not exposed to the action of reducing gases, and upon solution it evolved almost exactly the same amount of gas as the specimen which had been prepared in glass and ignited in porcelain. (See Experiments 37 and 38.)

Experiment 39, using zincic oxide prepared from the carbonate, was made to test again the accuracy of the method.

The weight of zincic oxide taken for each individual experiment is tabulated in the second column of the following table, and the third column indicates approximately the conditions used for the ignition of the different portions. The volume of gas given off on the subsequent solution of the zincic oxide in sulphuric acid is recorded in the fourth column, while the fifth contains the same data reduced to the standard of ten grams of zincic oxide. The sixth column contains a record of the analyses of the gases, and the seventh supplies information upon a few minor points connected with individual results.

[1] Erdmann: Ann. der Phys. Pogg. **62**, 611; Morse and Burton: This Journal **10**, 311-321.

No. of Exp.	Weight of Zincic Oxide.	Time and Temperature of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of ZnO.	Analysis of Gas by Volume.	Remarks.
	grams.		cc.	cc.		
1	1.375	Blast-lamp.	1.6	12.0		
2	1.19	"	1.45	12.2		
3	1.225	"	1.53	12.5		
4	1.1	"	0.00	00.0		From carbonate.
5	1.05	"	2.1	20.	$CO_2 = 2.0\%$	
6	1.08	"	2.1	19.4	$O_2 = 55.5$	
7	1.075	"	2.15	20.	$N_2 = 42.5$	
8	1.27	240° C.	0.00	00.0		Gave test for nitrates.
9	1.005	Bunsen flame.	.70	7.0		
10	1.065	"	.78	7.3		
11	1.22	Blast-lamp Hempel furnace.	.58	4.7		
12	1.91	"	.92	4.8		
13	1.05	Water-blast Hempel furnace.	.20	1.9		Made from basic nitrate.
14	1.07	Water-blast furnace 30 min.	.75	7.0		Fourth series.
15	1.00	"	.71	7.1		
16	1.02	Blast.	1.52	14.9	$CO_2 = 1.3\%$ $O_2 = 53.8$ $N_2 = 44.8$	
17	1.10	Water-blast Furnace 2 hr.	.35	3.2	$O_2 = 9.1$ $N_2 = 90.9$	Partly reduced.
18	1.20	" 3½ "	1.12	9.1		18–21 heated in double crucible by water-blast in furnace. Samples removed from time to time.
19	1.06	" 5 "	.83	7.8		
20	.85	" 6 "	.46	5.4		
21	.92	" 6½ "	.53	5.8		
22	1.07	Furnace 6½ hr. Oxygen flame, 15 min.	.42	3.9	$CO_2 = 0.0\%$ $O_2 = 16.9$ $N_2 = 83.1$	Layer next the silicate.
23	1.125	The same.	.48	4.3		Upper layer.

No. of Exp.	Weight of Zincic Oxide.	Time and Temperature of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of ZnO.	Analysis of Gas by Volume.	Remarks.
	grams.		cc.	cc.		
24	1.03	Oxy. fl. 15 min.	.24	2.3	$O_2 = 16.7\%$ $N_2 = 83.3$	Partially reduced and reoxidized.
25	1.105	" 30 "	.19	1.7		Reduced more than Ex. 24 and reoxidized.
26	.72	White heat 20 min.	.33	4.6	$CO_2 = 0$ $O_2 = 24\%$ $N_2 = 76$	White after ignition.
27	1.0125	White heat 35 min.	.45	4.4		" "
28	1.05	Water-blast ½ hr.	.42	4.0		Fifth Series.
29	1.019	1½ hr.	.37	3.6		
30	1.34	Bunsen Flame 30 min.	.28	2.10		Probably contained nitric acid.
31	1.05	Water-blast 30 min.	.97	9.2		
32	1.0035	Water-blast 1 hr.	.68	6.8		
33	.9765	1½ hr.	.63	6.4		
34	1.03	Water-blast ½ hr.	.175	1.7		Partially reduced.
35	1.08	½ hr.	.35	3.2		Less reduced.
36	1.50	20 min.	.82	5.46		Possibly reduced in part.
37	1.004	1½ hr.	.68	6.8		
38	1.018	2 hr.	.68	6.7		
39	1.00		0.00	0.00		Prepared from carbonate.

It is evident that we are dealing here with a phenomenon similar both qualitatively and quantitatively to that observed in the case of copper. Zincic oxide prepared from the nitrate occludes a very appreciable quantity of nitrogen and a somewhat variable quantity of oxygen. Continued application of heat tends to drive out both gases, the oxygen being less firmly held than the nitrogen; but the highest heat which we were able to obtain was insufficient

wholly to eliminate either gas. Under like conditions, specimens of zincic oxide made from zincic nitrate which had been obtained in a number of different ways appeared to hold approximately the same amounts of gas. It is almost, if not quite, impossible to prepare the oxide in this manner in a state wholly free from solid impurities taken from the containing vessel during the ignition of the purest possible zincic nitrate. The effort was made in the preceding series of analyses to prepare samples which must contain wholly different kinds of impurities. The fact that these different samples contained almost equal amounts of gas shows with reasonable certainty that the impurities are not responsible for the occlusion.

It is noticeable that the oxide obtained at a very low temperature, which still contained traces of zincic nitrate, contained little or no occluded gas (Experiments 8 and 30); also that six specimens which had been suspected of partial reduction contained much less gas than similar material free from this suspicion (Experiments 17, 24, 25, 34, 35, and 36).

Nickelous Oxide.

The series of experiments with nickelous oxide led to results not unlike those with zincic oxide. In this case sulphuric acid proved unsatisfactory as a solvent, and hydrochloric acid was adopted. A solution containing about 20 per cent. of hydrochloric acid gas was freed from air by continued boiling, rapidly cooled, and run into the tube containing the oxide of nickel. On account of the very slow action of the cold acid the tube was warmed after exhausting the air as usual. The gas set free was measured as before.

In order to prove the accuracy of the method a gram of zincic oxide prepared from the carbonate was dissolved in hot hydrochloric acid in precisely a similar way. No trace of gas was evolved during this solution.

It was thought unnecessary to make a series of experiments as elaborate as that made with the zincic oxide. Nickelous nitrate was evaporated to dryness in porcelain and ignited fifteen minutes in a blast-lamp and then a number of hours over a Bunsen burner in the furnace. (Analysis 1, below.)

A part of the nickelous oxide remaining was further ignited for two hours in the furnace by means of the water-blast. This was

used for the second analysis. A portion of the latter was ignited again in the furnace at the highest temperature we could obtain, by the addition of oxygen to the flame for about fifteen minutes, until the bottom of the outer crucible as well as the platinum foil between the two crucibles was melted away. The arrangement of data in the table is similar to that already described.

No. of Exp.	Weight of Oxide.	Vol. of Gas evolved.	Vol. of Gas calc. for 10 gr. NiO.	Analysis of Gas by Volume.
1	1.14 grams	.469 cc.	4.11 cc.	$O_2 = 12.25$ per cent. $N_2 = 87.75$
2	.997	.34	3.41	
3	1.13	.35	3.09	$O_2 = 8.8$ $N_2 = 91.2$

Magnesic Oxide.

The experiments with the oxide of magnesium led to very unexpected results, the amount of gas evolved upon the solution of this compound being five to twenty times as much as was obtained from zincic oxide, and over twenty-five times as much as from the oxide of nickel. More difficulty was found in decomposing the nitrate than before, and the remaining oxide was in a much harder and more compact state, and consequently more difficult to pulverize. The process used was similar to that employed in the case of the other oxides.

Magnesic nitrate made from pure nitric acid and magnesic carbonate of commerce was evaporated to dryness in porcelain. The residue was pulverized in an agate mortar, heated by means of the blast-lamp in a covered porcelain crucible, and cooled over calcic chloride. For a parallel experiment, a portion of the original carbonate was converted into the oxide by simple ignition, the magnesia formed in this way evolving only an extremely small amount of gas upon solution (Experiment 2 below).

A third portion of magnesic nitrate was made from pure magnesium ribbon and pure nitric acid, and the oxide was obtained from this salt by evaporation and ignition in porcelain as usual (Experiment 7).

Sulphuric acid was used for the solution of the magnesic oxide, as in the case of zincic and cupric oxides. The following table explains itself.

No. of Exp.	Weight of Oxide used.	Temperature and Time of Heating.	Volume of Gas evolved.	Volume of Gas calc. for 10 gr. of MgO.	Analysis of Gas.	Remarks.
	grams.	Blast-lamp,	cc.	cc.		
1	.50	30 min.	5.45	109.	$O_2 = 66.6\%$ $N_2 = 33.4$	
2	about 1.0	" 1 hr.	.05	.5		Made from carbonate.
3	.50	" 1¼ hr.	5.86	117.2	$CO_2 = 5.98$ $O_2 = 53.7$ $N_2 = 40.29$	Analyses made from one sample of oxide heated under different conditions. 1, 3, and 4 gave tests for nitrates with ferrous sulphate; 5 and 6 did not.
4	.25	" 2¼ hr.	2.31	92.4	$O_2 = 47.6$ $N_2 = 52.4$	
5	.25	" 3¼ hr.	2.31	92.4	$CO_2 = 2.2$ $O_2 = 38.9$ $N_2 = 58.9$	
6	.25	Oxygen-blast, 20 min.	2.04	81.6	$O_2 = 34.3$ $N_2 = 64.2$	
7	.25	Water-blast, 1½ hr.	2.31	92.4	$CO_2 = 1.5$	

The amount of gas occluded by magnesic oxide is thus much greater than that occluded by the oxides of copper, zinc, and nickel. The quantities of carbon dioxide recorded in the table are undoubtedly far from accurate, since the gas was collected over water. It is interesting to note that the amount of nitrogen evolved by the oxide upon going into solution was slightly increased up to a certain point by the increasing time and heat of the ignition, while the amount of oxygen was rapidly diminished.

No. of Exp.	Volume of Nitrogen found in 1 gram of MgO.	No. of Exp.	Volume of Oxygen found in one gram of MgO.
1	3.6 cc. Gas.	1	7.2 cc. Gas.
3	4.72	3	6.3
4	4.84	4	4.4
5	5.44	5	3.6
6	5.24	6	2.8

The Oxides of Cadmium, Mercury, Lead and Bismuth.

These oxides, the only other suspected ones which could be easily analyzed by the method in hand, all yielded negative results. The oxide of cadmium was distinctly crystalline, and contained only the merest trace of gas. The oxides of mercury, lead and bismuth obtained by the ignition of the corresponding nitrates also appeared to contain no occluded gaseous impurity.

Unfortunately, the oxides of antimony, iron, and a number of other metals, are not sufficiently soluble in acids to test with ease their power of occlusion by this method. It seems probable that interesting results might be obtained from them; hence in the near future other methods will be tried here, with the hope of determining if these oxides also occlude gaseous impurity.

Theoretical Considerations.

From the fact observed with both copper and zinc, that oxides which still contain a trace of nitrates, as well as those made from the carbonate, retain no imprisoned gas, it is readily inferred that the decomposition of a trace of nitric acid is alone responsible for the impurity. It is natural that this last trace of nitric acid should be confined below the surface, whence the gases resulting from its ultimate decomposition would find it hard to escape. On this supposition it is not unnatural that zincic oxide which has been partly reduced, and hence somewhat disintegrated, should contain less occluded gas than that which has not been thus reduced. Moreover, since magnesic nitrate is harder to decompose than the other nitrates, and the oxide is more compact, we should expect to find more gas occluded in this case than in the others. All these inferences agree with the facts. The difference in the rate of expulsion of the oxygen and of the nitrogen is interesting, and less easy to explain.

The negative results observed with a number of metals lead one to conclude that the physical condition of the oxides in these cases was so porous that even the last traces of nitrogen were allowed to escape. Indeed, cupric and zincic oxide made from very finely divided basic nitrates, obtained from aqueous solution, contained much less gas than samples which were obtained in a more compact condition by the direct ignition of the normal nitrate. This fact shows how much depends upon physical conditions.

It must be borne in mind that the occlusion of gases noted in this paper is a very different phenomenon from the retention of undecomposed oxides of nitrogen alluded to by Marignac,[1] Morse and Burton, and others. Nitrogen present in the state of gas could of course give no test with sulphanilic acid and naphthyl-

[1] "Il est probable que l'oxyde de zinc et la magnésie ne sont pas les seuls oxydes qui retiennent aussi énergiquement des composés nitreux, lorsqu'on les prépare par la calcination de leurs azotates." Ann. Chim. Phys. (6) 1, 311, foot-note.

amine, or any other test for oxidized nitrogen. It is evident that the phenomenon we are now studying, like the other just spoken of, may be a very serious cause of error in many of the published determinations of atomic weights; these would hence appear lower than their true value, because of the extra material which is calculated as oxygen.[1] Before any quantitative results obtained in this way can be accepted as authoritative, definite proof must be brought forward of the absence of this source of error. It is to be hoped that the able experimenters who have recently worked upon zinc, nickel, magnesium and similar metals have preserved typical specimens of their final products. If this is the case, nothing could be easier than to determine the amount of occluded gas, if any is present, and to apply the necessary correction.

As long ago as 1887 one of us was engaged, through the suggestion of Professor Cooke, upon an investigation of the atomic weight of zinc depending upon the analysis of zincic bromide. The work was discontinued because of the many publications upon this subject which appeared before it could be completed. Since the results recorded in this paper appear to indicate that the last word has not yet been said upon the subject, the investigation of zincic bromide and chloride is now being continued in this Laboratory.

THE EFFECT OF PLATINUM IN IRON SOLUTIONS.

By R. W. Mahon.

When the residue of an iron ore insoluble in acid is fused in platinum with sodium carbonate, a quantity of platinum is imparted to the subsequent solution of the fusion in water and hydrochloric acid. When the fusion is made with about 7 grams of sodium carbonate in a 25-cc. crucible with clean bright surface, fusing before the blast-lamp for a few minutes, the loss in weight

[1] The following are the elements whose atomic weights have been determined by means of the oxide made through action of nitric acid: Hydrogen (cupric oxide), Magnesium, Aluminium, Vanadium, Manganese, Nickel, Cobalt, Copper, Zinc, Gallium, Selenium, Tin, Antimony, Tellurium. See Meyer and Seubert: Atomgewichte, pp. 17–42; also for Nickel, Krüss: Z. anorg. Chem. **2**, 235; for Zinc, Morse and Burton: This Journal **10**, 311–321; for Magnesium, Burton and Vorce: This Journal **12**, 219; Chem. News **62**, 267.

of the crucible for one fusion is about 0.0008 gram. The presence of this much platinum when estimating iron by titration with potassium bichromate, after reduction by stannous chloride, dilution and addition of mercuric chloride in excess, is troublesome. Stannous chloride added to the hot hydrochloric-acid solution of ferric and platinic chlorides first reduces the iron and then the platinum. The solution which becomes gradually colorless during reduction of the iron to the ferrous state, again takes on a yellow tinge, due to the trace of platinous chloride formed. This minute quantity of platinous chloride colors the solution on account of the formation of one of the two compounds of platinous and stannous chlorides described by Kane,[1] being the one containing the most tin. The addition of mercuric chloride after dilution gives a solution with a precipitate suspended in it, the whole sometimes having a tinge of color; instead of giving, as in absence of platinum, a colorless solution with pure white mercurous chloride in suspension. Platinum being present, the titration with bichromate causes first the disappearance of color and next the oxidation of ferrous chloride, until finally drops taken from the solution no longer give a blue color with potassium ferricyanide. After this point has been reached a recurrent bluing is sometimes met with, especially if the solution stand a moment and a drop then removed be tested. Sometimes this recurrence is rapid enough to amount to a continuous coloration.

The interference of platinum in this method for iron estimation is well known to many, although there is no published reference to it. I have therefore sought to study the reactions which take place, and to devise a method for overcoming the difficulty.

In his study of the chloroplatinites, Nilson[2] speaks of the impossibility of preparing ferric chloroplatinite, as ferric chloride and chloroplatinous acid form ferrous chloride and ferroplatinate and ferriplatinate. The part of this reaction which is of interest in the present connection is the reduction of the ferric chloride by platinous chloride. The solution, acid with hydrochloric acid, obtained in the course of analysis just before dilution, is clear, and, as has been stated, of a yellow tint in presence of platinum; it remains clear upon dilution. If less acid were present and the solution much more copiously diluted, the platinum-tin chloride would be decomposed and precipitated, as described by Kane,

[1] Phil. Mag. [3] **41**, 399. [2] J. prakt. Chem. [2] **15**, 282.

yet, even for slight acidity and extreme dilution, this reaction can be seen only when the quantity of platinum occurring in an analysis is several times as great as is usual in analyses of this kind. When then, in the course of analysis, mercuric chloride is added to the diluted solution, in addition to the mercurous chloride formed, the platinum is precipitated. The color of the solution with the precipitate in suspension is due to the platinum precipitate, the solution if filtered at this point being colorless. The quantity of platinum present in an analysis is too small to impart much color to the whole mass of mercurous chloride precipitated.

If to a solution of platinic chloride, strongly acid with hydrochloric acid, stannous chloride be added and then mercuric chloride in excess, three cases are to be distinguished:

1. The stannous chloride is added only in sufficient quantity to convert the platinic to platinous chloride.—The addition of mercuric chloride produces no precipitate.

2. The stannous chloride is added in six times the amount just mentioned, or in some intermediate amount.—The solution takes on a deep red tint if an appreciable quantity of platinum is used. The addition of mercuric chloride changes the red to yellow, and the solution then deposits a black precipitate.

3. The stannous chloride is added in more than six times the first mentioned amount.—In an actual analysis, the quantity of platinum being so minute, the stannous chloride will have been thus added. By close observation and working rapidly, the following changes are seen to take place upon addition of mercuric chloride: The color of the solution changes from red to yellow; mercurous chloride is precipitated. If this is filtered out the yellow filtrate deposits a black precipitate. These precipitates first come down of a dark brownish-red color and then turn black. This change of color from reddish-brown to black is best seen when using a minute quantity of platinum. The same precipitate,[1] evidently mercurous chloroplatinite, was obtained by Nilson on adding mercurous nitrate to potassium chloroplatinite. He describes it as amorphous, dark brown, and rapidly turning black in the mother-liquor. Mercurous chloroplatinite is easily soluble in ferric chloride, yielding ferrous chloride, platinic chloride and mercurous

[1] In a modification of the stannous-chloride method which I have suggested (This Journal **15**, 360) the end-reaction is incorrectly described. The first few drops of stannous chloride in excess over that needed to reduce the iron, acting upon the platinum-mercury indicator, precipitate mercurous chloroplatinite.

chloride; the platinic salt then acting upon the mercurous to form mercuric chloride, and the platinous chloride formed reducing a further quantity of ferric chloride.

The same changes take place in an iron-estimation. The stannous chloride will have been added in sufficient excess to reduce all the iron and platinum, and to cause the precipitation of mercurous chloride and mercurous chloroplatinite—the conditions described in 3. At the commencement of the titration the tinge of color disappears, because the first few drops of bichromate oxidize some of the iron to ferric chloride, which then acts upon the mercurous chloroplatinite, forming platinic chloride, and adding a minute quantity of mercurous chloride to that already present. The platinic chloride at the moment of its formation is again reduced by mercurous chloride. The titration proceeds, and the same cycle of operations is repeated, until finally all the iron is oxidized, and the mercurous chloride all dissolved as mercuric. Thus a small quantity of platinum may introduce a large error into the estimation.

Although troublesome, the presence of platinum is not fatal to accuracy. From many iron ores when reduced to an impalpable powder, hydrochloric acid of 1.20 specific gravity dissolves practically all of the iron, leaving an amount so small that it may be disregarded even in accurate estimations. This is of course not always the case, and when a fusion must be made, the simplest way of avoiding error is to add stannous chloride with care, and cease when the color due to ferric iron has disappeared, and before that due to platinous chloride has begun. Another way is first to precipitate the iron in the fused and dissolved residue by means of ammonia, filtering on a small filter, and, after thorough washing, redissolve in hydrochloric acid and hot water, receiving in the beaker of precipitation. Thus a solution is obtained entirely free from platinum.

The following are four determinations of iron in the same ore. In Nos. 3 and 4 the causes leading to error were purposely exaggerated, although no platinum was introduced except that derived from the crucible.

	Percentage of iron		
	In the solution.	In the fusion.	Total.
1.	57.57	1.20	58.77
2.	57.57	1.20	58.77
3.	57.57	5.84	63.41
4.	57.67	4.83	62.50

The causes leading to error when the platinum has not been separated before titration are: 1. The presence of much platinum introduced by protracted fusion; 2. A large quantity of free hydrochloric acid; 3. The addition of a large excess of tin.

It is desirable that fusion should be thorough, in order that decomposition may be perfect, and that a considerable quantity of hydrochloric acid be present to obtain sharp reactions. A distinct excess of tin has the advantage of certainty of complete reduction, and at a lower temperature, thus giving a cold solution finally after dilution.

The preliminary separation of platinum as described above is much to be preferred to the other way of working.

Contribution from the Laboratory of General Chemistry, University of Michigan.

ON THE ACTION OF SODIUM ON ACETONE.

By Paul C. Freer.

Some three years ago I published two preliminary notices[1] describing the reaction which takes place when sodium is brought in contact with acetone mixed with a large volume of absolute ether, and at a later date I prepared a more extended paper on the same subject.[2] Since that time I have been able, by means of improved apparatus, to obtain large quantities of the products of the reaction at one operation, and as a consequence have been able much more accurately to determine the real changes which take place. As a result of these further investigations it has been proven that the sodium acetone formerly described as a uniform body, in reality consists of that substance mixed with a number of others.

In order definitely to settle the fact that a molecule of acetone contains a hydrogen atom that is replaceable by one of sodium, it is necessary to prove, in the first place, that hydrogen is evolved when sodium is brought in contact with the liquid in question, and, in the second place, that acetone can once more be separated, by addition of dilute acids, from the compound formed by this

[1] This Journal **12**, 355; J. prakt. Chem. [2] **42**, 470. [2] This Journal **13**, 319.

means. A long time ago Löwig and Weidmann[1] studied the action of potassium on acetone, discovering that the reaction between the metal and pure acetone is of such violence that if great care is not exercised the liquid takes fire; yet this catastrophe could be averted by sufficient cooling. No permanent gas is, however, developed. Fittig,[2] at a later date, observed that sodium attacks acetone with considerable energy, producing a flaky-white precipitate, which soon becomes brown upon the surface, but made no observations in regard to a gas which may possibly be developed. This investigator studied the action of ethyl iodide on the products of the reaction; he distilled the mixture and discovered that only ethyl iodide and acetone passed over, whereas, upon heating the solid remainder, a thick oil that soon deposited crystals of pinakon, was produced. Subsequently Städeler[3] also observed that anhydrous acetone develops no gas when brought in contact with sodium. In my former papers on this subject I have shown that acetone, if diluted with an indifferent solvent, liberates hydrogen when acted on by sodium. In spite, then, of this previous work I have repeated the experiments in a most careful manner, and have come to the conclusion that although pure acetone when treated with sodium liberates no trace of gas, nevertheless, if it is mixed with absolute ether, ligroïn or xylene it evolves hydrogen in increasing proportion with increasing dilution; the quantity of gas produced by dissolving a constant quantity of sodium reaching a maximum at a ratio of 1 of acetone to 100 of solvent, this maximum being about 62 per cent. of the amount calculated by theory. It is actually true, therefore, that acetone, provided the proper preliminary precautions are taken, will liberate hydrogen when brought in contact with sodium; when, however, no diluent is present, all of the gas is immediately used up for purposes of reduction, and even under the most favorable circumstances a considerable portion thereof disappears. The compounds produced by this reaction naturally contain sodium isopropylate and sodium pinakonate, in addition to acetone sodium, and it is also possible, as will be shown below, that the sodium compounds of mesityl oxide and of phoron are also formed—at least it has been shown that all of these substances are liberated from the white, flocculent precipitate on the addition of dilute acids.

[1] J. prakt. Chem. **21**, 54; Ann. der Phys. Pogg. **17**, 309. [2] Ann. Chem. (Liebig) **110**, 23.
[3] *Ibid.* **111**, 277.

In order to determine whether the sodium in acetone sodium is contained in a natroxyl group or is attached to carbon, I have studied the action both of benzoyl chloride and of ethyl chlorcarbonate on the mixture of sodium compounds, and, as will be seen from that portion of this paper which deals with the experimental work, the results obtained with the former reagent admit of the definite conclusion that the sodium in sodium acetone is in reality attached to oxygen, and that therefore the substance in question possesses the following formula: $CH_3-CONa=CH_2$, so that it is to be regarded as the sodium compound of β-allyl alcohol.

Experimental Part.

Determination of the Relative Quantity of Hydrogen which is evolved when Sodium acts upon Acetone.

The acetone which was used for all of these and many of the following experiments was prepared from the sodium bisulphite compound. It was dehydrated by repeated distillation over fused calcium chloride, followed by shaking with an excess of phosphoric anhydride,[1] pouring off the liquid, fractioning, and finally twice distilling the liquid, which is presumably perfectly free from water, after the addition of about 0.5 gram of sodium before each operation. That portion which had a boiling-point of 56.5°–57.5° was used exclusively, and was always kept over fused sodium sulphate.[2]

It very soon became apparent that Löwig and Weidmann's, as well as Städeler's, statements were correct, namely, that pure acetone develops no hydrogen when brought in contact with the alkali metals, as the following experiment proves: 0.5 gram of pure sodium, finely powdered under toluene, was sealed in a small glass bulb also filled with that liquid, and the bulb was then placed in a tube containing pure acetone. The tube was then drawn out to a bent point 10 cm. in length, which was sealed after cooling the

[1] This operation was twice repeated.

[2] When, at a later period in the research, it was discovered that some isopropyl alcohol is always formed when sodium is dissolved in acetone, it occurred to me that the criticism could be made that the evolution of hydrogen might be due to isopropyl alcohol which might be liberated when the acetone, previously treated with sodium, was distilled. Although this seemed extremely improbable, as in all likelihood the isopropyl alcohol would be present in the form of sodium isopropylate, I nevertheless repeated all of the work, using acetone which had been dehydrated by shaking four times with phosphoric anhydride, pouring off and distilling. There is no doubt that this substance is perfectly anhydrous, although the use of sodium was entirely avoided.

entire apparatus to 0°. The glass bulb was then broken by shaking and, after the completion of the reaction, the temperature was once more brought to 0°, and the tip of the enclosing tube was opened under water. The pressure was found to be unchanged, and hence no gas had been liberated. Entirely different results are observed, however, if the acetone has been diluted by means of some indifferent solvent before adding the metal.

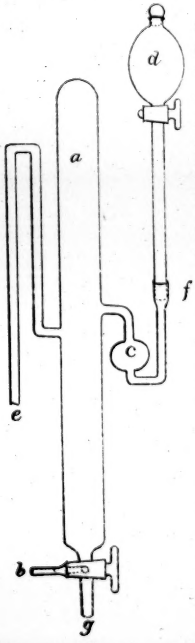


FIG. 1.

In order accurately to determine the amount of gas which is liberated under differing experimental conditions of solution I finally constructed the following apparatus, which admirably answered my purpose: About 0.1 gram of sodium is cut and weighed under liquid paraffin and then placed in the bulb *c* connected with the tube *a* (Fig. 1), the latter having previously been completely filled with pure and perfectly dry xylene; the dropping-funnel *d*, which is connected by a gas-tight glass joint at *f*, is now connected and all of the air expelled from it and from the stem by addition of xylene and repeated shaking. Acetone of any dilution required can now be added through *d*, while the gas passes from *c* and collects in the tube *a*. After the reaction is complete a pressure-bottle is connected with *e*, the dropping-funnel is removed and the tube stoppered at *f*. The whole apparatus is now inverted and the hydrogen is forced from *g* through a washing-train[1] from which the air has previously been expelled by a current of pure carbon dioxide entering at *b*, and it is finally collected over caustic potash in an ordinary Schiff's azotometer. The quantity of hydrogen liberated was determined after each

[1] The washing-train consisted of three Geissler potash-bulbs and a long tube filled with shavings of solid paraffin. The first two potash-bulbs were charged with liquid paraffin, the third with conc. sulphuric acid. All of the xylene vapor and other organic matter is removed from the hydrogen by this means.

experiment by explosion in a Bunsen eudiometer;[1] it was not necessary, therefore, to exercise the greatest care in expelling all air from the apparatus before collecting the gas.

The results of five determinations, with successively increasing dilution of acetone, are given in the following table; as the others, as a rule, agreed very well with the ones given below, it was not deemed necessary to take up space by adding more.

	Quantity of Sodium.	Proportion.	Found, Hydrogen.	Calculated.	Percentage.
I.	0.1078 gram.	Undiluted acetone added to apparatus filled with xylene.	3 cc.	52.1 cc.	5.77
II.	0.0990 "	Equal parts of acetone and xylene.	11.7 "	47.8 "	24.5
III.	0.1000 "	1 acetone : 5 xylene.	13 "	48.3 "	26.9
IV.	0.1054 "	1 : 25	25.93 "	50.7 "	51.16
V.	0.1078 "	1 : 100	32.71 "	52.1 "	62.7

These experiments furnish the final proof that acetone when treated with sodium in reality liberates hydrogen. As has been remarked before, the entire quantity of gas, if the acetone be pure, is used for purposes of reduction; the amount which is set free, however, increases with increasing dilution until it reaches a maximum at a ratio of about 1 : 100. At this point the action becomes quite slow, so that the sodium requires at least a week for complete disappearance. If the relative quantity of diluent is made still greater the formation of sodium acetone goes on so slowly that secondary reactions render the results inaccurate, if indeed the sodium is attacked at all after the first few minutes. It seems improbable, therefore, that the theoretical quantity of hydrogen can be obtained;[2] nor indeed is this at all necessary, as the main fact *that hydrogen is really set at liberty* is the only one of vital importance.

[1] A small ball of solid potash was thrust into the gas space after each explosion, in order to detect any carbon dioxide which might be present; the figures given belong only to determinations in which no contraction, owing to carbon dioxide, took place.

[2] In my former paper I stated that the theoretical quantity of hydrogen can in reality be obtained; the determinations referred to at that time were, however, made with very volatile petroleum ether as a diluent, the apparatus used was not perfectly adapted to the purpose, nor was care taken to determine the absolute quantity of hydrogen by explosion after each experiment.

The Products which are formed by the Action of Sodium on Acetone.

If finely powdered sodium is covered with a great excess of absolute ether, and acetone (purified as indicated above, and also diluted with five times its volume of ether) is then gradually added, reaction begins at once, hydrogen passes off and, after a while, the ether comes to a boil, while at the same time a white, flocculent substance, having somewhat the appearance of precipitated aluminium hydroxide, separates. When this body is brought in contact with the air it instantly assumes a deep red color and is decomposed; for that reason all operations in which it is concerned must be conducted in an atmosphere of pure hydrogen carefully dried with phosphoric anhydride. In order to obtain the sodium compound in any desired quantity[1] I made use of the apparatus described below.[2]

A flask, *a*, of 750 cc. capacity, having a flat bottom and wide neck, was fitted with a quintuple-bored rubber stopper. Pure hydrogen can be passed by means of the double-bored stopcock *d* at will, either through *a* or through *b*, which latter flask is intended to contain the pure and dry ether necessary for washing the precipitate when it is collected in the funnel *f*, into which the products formed in *a* are aspirated by a Chapman pump attached to *c*. The substances after being collected in *f* are by suction freed from liquid as much as possible and then repeatedly washed with the ether which is forced over from *b*, and finally the remaining traces of the latter liquid are removed by passing a rapid current of dry hydrogen through the apparatus for more than an hour.[3] If it is found necessary to isolate products which are soluble in ether, a second flask, similar to *b* (but containing a triple-bored rubber stopper, the third hole of which is con-

[1] In my former paper I stated that the sodium compound was rapidly filtered, washed with absolute ether and then dried on a porous plate in an atmosphere of hydrogen. Some reddening always took place during the operation and, furthermore, the quantity of acetone sodium isolated at one time was so small that I was compelled to be satisfied with a sodium determination and with the mere qualitative proof that acetone was produced from it by the addition of dilute acids.

[2] I wish to take this opportunity of thanking Mr. R. R. Putnam for his suggestion of the apparatus which was used.

[3] Of course all of the air must be expelled from the apparatus by means of a current of hydrogen, before the acetone is brought in contact with the sodium. The rapid escape of the gas through the Liebig condenser, and consequent introduction of air, is prevented by closing the end of the latter instrument by means of a mercury valve. The liquid is kept constantly stirred during the reaction, by means of the rod *g* which is attached to a small water-motor.

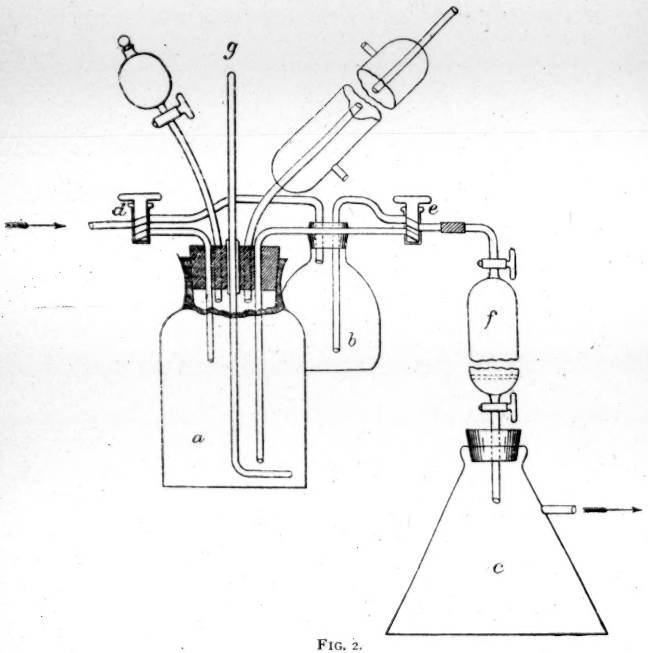


FIG. 2.

nected with a worm condenser), is introduced between *a* and *f*. If the precipitate in *a* is allowed to settle, the supernatant liquid can then be sucked over into this additional receiver, which operation may be repeated as often as necessary by successive additions of ether through the dropping-funnel. The dissolved products are finally isolated by gently heating and so evaporating the solvent. The funnel-cylinder *f* is closed above and below by means of glass stopcocks, so that when the latter are closed the precipitate can be removed and weighed without at any time being allowed to come in contact with a trace of air. As the research advanced it became apparent that the sodium compounds

produced were of two kinds, namely, those soluble and those insoluble in ether; so that the separation of the two became of vital importance. The soluble portion, when pure, is a yellowish powder which instantly reddens when brought in contact with the air, the oxidation sometimes being so violent that the entire mass takes fire; the insoluble part, on the other hand, is white, and when thoroughly washed shows much less tendency to change.

The Products of the Action of Sodium on Acetone which are Insoluble in Ether.

Several sodium determinations of samples of the insoluble portion were made; these invariably demonstrated that a slight excess of sodium above the amount which is required by theory to be present in acetone sodium, was to be found.[1] The proportion of the metal is, however, always very nearly that which would be found in combination provided one atom of sodium were to react with one molecule of acetone, and from this it follows that if the sodium compound is in reality a mixture, and if *sodium pinakon is present* in this mixture, the latter substance must exist as the disodium derivative. The calculated percentage of sodium in pure sodium acetone is 28.75 per cent. I found in the insoluble portion of the products of the reaction 30.6, 31.42 and 31.2 per cent.[2] The excess of sodium is undoubtedly due to some decomposition which takes place, even if the entire work has been conducted in an atmosphere of pure hydrogen; that this is probably the case is shown by the fact that those samples which had suffered some delay during their preparation were always the ones which contained relatively the greatest quantity of sodium.

In order to identify the substances which are present in the insoluble sodium compound, ten samples of the product, entirely free from ether or acetone, each prepared by treating 2.5 grams of finely powdered sodium with an excess of well diluted acetone,[3]

[1] Beckmann [Ann. Chem. (Liebig) **266**, 19] found that the sodium contents of acetophenone sodium was always about 2.5 per cent. *less* than the calculated quantity. This investigator also states that no permanent gas is developed when sodium acts on acetophenone; if all of the hydrogen were used for purposes of reduction it would follow that the quantity of sodium would be less than the theory demands.

[2] These figures are selected from a number of analyses which gave similar results.

[3] Great care was taken thoroughly to remove all acetone from these samples by several decantations with pure ether before sucking the precipitate into the glass-tube filter (*f*, Fig. 2), and then by washing the collected precipitate repeatedly with the same liquid. The current of hydrogen was then passed through the filter until absolute certainty was reached that every trace of liquid had been evaporated.

were, as soon as the reaction was complete, treated with a slight excess of very dilute ice-cold acetic acid; this instantly dissolved the substance, the solution being of a light straw-color and only very slightly turbid. All of the acidified portions of liquid were now united, neutralized and distilled until no iodoform reaction could be obtained with a sample of the residue in the retort. The distillate was then supersaturated with potassium carbonate, again distilled, and this operation repeated until only about 75 grams of fluid were left, which, upon addition of the same solid, separates into two layers, the lower one a colorless solution, the upper one a straw-colored oil. The latter was allowed to stand over solid potassium carbonate, and was then carefully fractioned, with the following result: about one-half passes over between 65° and 83°; the thermometer then rapidly rises to 165°, between which temperature and 190° the greater part of the remainder distils, while the few drops of residue boil between 200° and 220°.

The low-boiling portion was now carefully treated with a concentrated solution of sodium bisulphite, upon which addition the entire mass apparently solidifies into the characteristic shiny plates of acetone sodium bisulphite. When, however, these crystals are pressed out, a considerable quantity of mother-liquor separates, the latter forming two layers, the lower one of which is an aqueous solution of acetone sodium bisulphite, the upper one an organic liquid. This liquid was separated and dehydrated by first distilling it several times over solid potassium hydroxide, and then by repeatedly fractioning, after the addition each time of a small piece of sodium. The entire quantity then boils between 81° and 81.5° (739 mm. pressure) and gives the following analytical data:

I. Twice fractioned over sodium—

Substance, 0.2038 gram; CO_2, 0.4290 gram; H_2O, 0.2380 gram.

Found: C = 57.5; H = 12.92 per cent.

II. Three times over sodium—

Substance, 0.2230 gram; CO_2, 0.4764 gram; H_2O, 0.2653 gram.

Found: C = 58.4; H = 13.16 per cent.

III. Four times over sodium[1]—

[1] The sodium evidently first in greater part attacks the ethyl alcohol to form sodium ethylate, and so, after repeated additions of this metal, and fractioning, only isopropyl alcohol is left behind. Pure isopropyl alcohol which has been treated in this way is *almost entirely* indifferent to sodium at ordinary temperatures, sodium isopropylate being formed *only when the liquid is warmed*. The question whether sodium does or does not attack a given substance, therefore, has no bearing on the question as to whether that substance contains an hydroxyl group or not.

Substance, 0.2550 gram; CO_2, 0.5586 gram; H_2O, 0.3102 gram.
Found: C = 59.75; H = 13.43 per cent.

Calculated for Isopropyl Alcohol.		Calculated for Ethyl Alcohol.	
C	60. per cent.	C	52.17 per cent.
H	13.3	H	13.17

These analyses prove, without doubt, that the isopropyl alcohol which was produced by reduction was mixed with some *ethyl alcohol;* however, as the acetone used was from the sodium bisulphite compound, and as the solvent was ether which was entirely free from alcohol, there is only one interpretation of the facts possible, namely, that ether is *not* an absolutely indifferent solvent in this and similar reactions.[1] I have repeated the above experiments several times and always with the same results. This conclusion is also borne out by the work with benzoyl chloride which is given below.

The filtered acetone sodium bisulphite which was separated from the isopropyl alcohol, was treated with a concentrated solution of sodium carbonate and fractioned; the entire quantity of the organic liquid which separated then boiled at 56.5° and proved to be pure acetone. The relative quantities of acetone and of isopropyl alcohol formed vary with the amount of ether which is originally employed as a solvent; under most favorable circumstances there is about twice as much acetone as isopropyl alcohol; under the most unfavorable, about equal quantities.

The fraction of the anhydrous distillate boiling between 165° and 190°, obtained from the decomposition of the insoluble sodium compounds by dilute acetic acid, was mixed with about three times its own volume of water and allowed to stand. The liquid soon becomes quite hot, and upon cooling solidifies to a mass of crystals which contains a few drops of a yellow oil; the latter was removed by washing with a little ether, while the solution thus obtained was united with the fraction boiling between 200° and 220°. The solid was now recrystallized from a little hot water, from which on cooling it separates to the last trace in large, transparent, quadrangular plates which effloresce in the air and finally evaporate at ordinary temperatures. These qualities are

[1] Absolutely pure ether, which apparently has no effect on sodium, will nevertheless be attacked by the metal after some time if placed in the sunlight. Ether over sodium should therefore be kept in the dark. (See also Beckmann: Ann. Chem. (Liebig) **266**, 9.)

so characteristic of hydrated pinakon that an analysis was deemed unnecessary.[1]

The high-boiling portion (between 200° and 220°) was finally fractioned, when it was found that the greater portion passes over between 206° and 212°, while a very small amount of a tar-like residue remained in the flask. This yellow oil is undoubtedly, in part, identical with the high-boiling phoron which was obtained by Fittig[2] by the action of quicklime on acetone, and by Städeler[3] when he treated the same substance with sodium, and which was subsequently compared by Kachler[4] with phoron obtained by other means, and described in his table comparing the properties of compounds having the formula $C_9H_{14}O$. However, my oil reacts only slowly and very incompletely with phenylhydrazine; evidently, therefore, there is only very little ketone present,[5] in comparison with a large quantity of a reduced body, but, as the amount of this reduced body, even after uniting the product of several operations, was not sufficient to warrant a careful separation, no analysis was made.[6] Mesityl oxide could not be found among the products produced by acidifying the sodium compounds.

That portion of the product of the action of sodium on acetone which is insoluble in ether consists, therefore, of *acetone sodium*, *sodium isopropylate*, and *disodium pinakonate* mixed with a small quantity of sodium ethylate. If the ether used in the initial operation is sufficient in quantity, then the greater part consists of acetone sodium, while sodium isopropylate and disodium pinakonate are present in about equal proportions.[7]

[1] The crystals were also converted into anhydrous pinakon by distillation over solid caustic potash; the oil so obtained possessed the very characteristic odor of anhydrous pinakon.

[2] Ann. Chem. (Liebig) **110**, 32.

[3] *Ibid.* **111**, 279.

[4] *Ibid.* **164**, 80.

[5] Perhaps it is $C_{12}H_{20}O$ (boiling-point 213° to 217°), formed by reducing mesityl oxide. *Vide* Claisen: Ann. Chem. (Liebig) **180**, 8.

[6] Only about 0.75 gram of this high-boiling body can be obtained by decomposing 30 grams of the sodium compounds.

[7] Beckmann and Paul (Ann. Chem. (Liebig) **266**, 18) believe that the sodium derivative of acetophenone is produced by two molecules of the latter substance reacting with two atoms of sodium, and assign to the sodium derivative an improbable formula which differs from that of disodium acetophenone-pinakon only in having one sodium atom attached to carbon instead of replacing a hydrogen atom in hydroxyl. They assume this more complicated structure to exist because no hydrogen is evolved during the reaction between sodium and acetophenone. In the case of acetone, however, hydrogen *is* evolved; the assumption that acetone sodium has a molecular formula which is double that which the simplest relationship calls for, is therefore unnecessary. Nevertheless, it is not impossible that *pinakon sodium* is not present in the

The Sodium Compound Soluble in Ether.

As has been mentioned above, there remains a yellow powder, which is oxidized with remarkable readiness, after completely evaporating the ether and acetone from the ethereal solution of the soluble sodium compound. In order to ascertain the nature of this compound, the product of each operation, as soon as finished, was acidified with ice-cold and very dilute acetic acid, and the liquids produced by ten such decompositions were united. As soon as the dilute acid came in contact with the powder, the latter dissolves and at the same time assumed a deep red color, which changed to yellow when an excess of acid had been added, while a brownish colored oil separated.[1] The solution, after the removal of the oil, gave an iodoform-reaction with iodine and ammonium iodide, so that the presence of acetone therein was beyond doubt.[2] The oil was isolated, dried over calcium chloride

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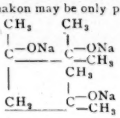
sodium compounds, for the pinakon may be only produced upon acidifying. A sodium compound having the structure  would be similar to that assumed to exist in the case of acetophenone sodium; one molecule of this substance might break down into one of pinakon and one of acetone when an acid is added. Such a theory is doubtful, however, because such a body would, presumably, be stable when acidified. Although its formation by addition to the unsaturated pair of carbon atoms in acetone sodium is not improbable, it may be present in the high-boiling portions. The fact that one portion of the sodium compounds derived from acetone is *soluble*, the other *insoluble*, shows that two different classes of such compounds are produced by the reaction, and, as the pinakon in conjunction with acetone always appears on acidifying the *insoluble* portion, it seems necessary to assume that a more complicated sodium compound exists in this part. The evolution of the large quantity of hydrogen during the reaction shows beyond doubt, however, that the greater portion of the sodium acetone is present in its simplest form, and this, most probably, in the soluble part.

[1] The ether-soluble compound is also instantly decomposed by water, the solution assuming a deep red color, while an oil, which is also red, separates. On acidifying, the solution changes to yellow and the oil to brown.

[2] During the course of this research I took occasion to review the various qualitative methods for proving the presence of acetone when mixed with isopropyl alcohol and pinakon. The usual iodoform-reaction in which sodium or potassium hydroxide is used is, of course, out of the question, as both isopropyl alcohol and pinakon would yield iodoform under similar circumstances. The acetone-test with precipitated mercuric oxide is also of no value when the presence of small quantities of acetone is to be proven, because mercuric oxide is noticeably soluble in caustic alkalies, and this solution, after acidifying, gives a very marked turbidity with stannous chloride; the solubility of the oxide is, however, not increased by the presence of isopropyl alcohol or pinakon. On the other hand, the iodoform reaction with iodine and an ammoniacal solution of ammonium iodide (Gunning: Ztschr. anal. Chem. **24**, 147) is very satisfactory. Neither isopropyl alcohol nor pinakon forms iodoform with this mixture, even if in contact with it for days; while acetone reacts after a very few minutes, even when very dilute. It must be remembered, however, that the condensation-products of acetone likewise produce iodoform when treated with this reagent. The formation of indigo with orthonitrobenzaldehyde is not always practicable, and the benzalacetone-reaction cannot be used to prove the presence of small quantities.

and fractioned: a small portion passed over between 100° and 140°; the thermometer then rose rapidly until it reached 200°, between which temperature and 220° about one-third of the remainder distilled; a considerable portion then boiled between 220° and 290°, the residue in the flask being a perfectly solid semi-transparent resin. The portion distilling between 200° and 220° was now refractioned under diminished pressure, the greater part boiling at 165° (90 mm.)[1]; the middle part of this fraction was analyzed:

Substance, 0.1793 gram; CO_2, 0.5145 gram; H_2O, 0.1788 gram.

	Calculated for $C_9H_{14}O$.	Found.
C	78.26	78.26
H	10.19	10.9

There is no doubt, therefore, that this portion of the oil possesses the formula $C_9H_{14}O$, and from its boiling-point and other properties it must be considered as being identical with phoron which is produced by the action of alkaline condensing-agents on acetone. As might be expected, this substance reacts readily with phenylhydrazine, and the same is true of the high-boiling portion (220°–290°), although no body with even an approximately constant boiling-point could be isolated from this part.

The acid solution which was obtained by treating the ether-soluble sodium compounds with dilute acetic acid and from which the oil above described had been separated, was neutralized with potassium carbonate and then treated exactly as has been described above in that portion of this article referring to the isolation of acetone and isopropyl alcohol from the solution obtained by similarly acidifying the insoluble portion. When the organic liquid had been entirely separated and freed from water it was fractioned: a small quantity passed over between 60° and 70°, and this part completely united with sodium bisulphite to form acetone sodium bisulphite. The higher-boiling portions consisted of mesityl oxide and a little pinakon. The organic liquids which can be separated from the aqueous solution are much less in quantity than is the oil described above, and it will be noticed that *no isopropyl alcohol* and but very little pinakon can be found among

[1] This fraction boils between 206° and 212°, ordinary pressure. My experience is identical with that of Fittig when he investigated the high-boiling products from the action of quicklime on acetone, and of Städeler when he produced the same body from sodium, namely, no substance with a perfectly constant boiling-point could be isolated.

the products of the decomposition by dilute acids of the sodium compounds which are soluble in ether, they being almost exclusively *condensation-products of acetone.*

There can scarcely be any doubt that the ether-soluble portion of the sodium compounds represents almost pure sodium acetone, and that the mesityl oxide, phoron and higher-boiling oils which are found after adding the acid, are produced by the intensely energetic action which takes place when the dry sodium acetone is acidified. That this is the case is shown by the fact that the dilute ethereal solution of this substance, after it is carefully acidified, contains only a very small quantity of mesityl oxide and no phoron; neither has the latter of these products ever been observed among the results of the action of chlorocarbonic ether or of benzoyl chloride on acetone sodium.[1]

The ether-soluble and -insoluble portions appear, when the work is carefully conducted, in about equal proportions; if the amounts of each which were produced in any one operation are added together, then, assuming that the ether-soluble portion is almost pure acetone sodium, the quantity of the latter body by far exceeds that of the sodium isopropylate and pinakonate.

The experiments detailed above show without doubt that a molecule of acetone contains a hydrogen atom which is replaceable by sodium, and, this point being settled, the next question to be solved is in regard to the structural formula of the sodium compound—whether the metal is attached to oxygen or to carbon. At first, as was described in a former paper,[2] I studied the action of ethyl chlorcarbonate on acetone sodium, but, as the reaction led to much more complicated results than the ones which I then supposed to be the true ones, I next chose benzoyl chloride, and indeed the latter reagent led to the most complete clearing-up of the case. For this reason I shall give a detailed description of the work with benzoyl chloride, reserving a short mention of the reactions with chlorcarbonic ether for the close of this article.

The Action of Benzoyl Chloride on the Products of the Reaction between Acetone and Sodium.

Three grams of finely powdered sodium are covered with 300 cc. of absolute ether and placed in the flask *a* of the apparatus

[1] That this is the case was shown in my former article on this subject: This Journal **13**, 321.

[2] Freer and Higley: *Ibid.* **13**, 322.

(Fig. 2); all of the air is then expelled by hydrogen, and an excess of diluted acetone gradually run in until all of the sodium has disappeared, the whole being meanwhile vigorously stirred by the water-motor. Somewhat less than the calculated quantity of pure benzoyl chloride—entirely free from benzoic acid and diluted with twice its own volume of ether—is then slowly dropped in: an instant and most violent reaction takes place and the ether comes to a boil (so that it is necessary from time to time to cool the flask with water) while at the same time the sodium compound assumes an orange color. After all of the benzoyl chloride has been added the whole is warmed for about an hour on a water-bath; the reaction is completed when the orange color has changed to the pure white of sodium chloride. The ethereal solution is then of a light straw-color. The results of ten such operations are united into one and worked up together. The whole is first shaken out several times with water and is then extracted with a solution of sodium bicarbonate until a sample of the latter separates nothing when acidified. The remaining fluid is then treated in the same way with sodium carbonate and finally with 10-per cent. sodium hydroxide; the extractions with each reagent are preserved and investigated separately.

The Portion of the Oil which is Insoluble in Alkalies.

The neutral products of the reaction which are now alone present in the ethereal solution are dried over fused calcium chloride, the ether evaporated, and the remaining brown oil, which possesses an odor resembling benzoic ether, is fractioned. The first distillation separates the fluid into a low-boiling portion (128°–133°) and a part passing over above 200°, while a high-boiling residue which decomposes on distillation remains in the retort. The oil boiling between 128° and 133° is mesityl oxide, mixed with a small quantity of a chlorinated body which it is impossible to separate by fractional distillation.

The product boiling above 200° was now carefully fractioned under diminished pressure; after a few drops of remaining mesityl oxide have been removed the thermometer rises rapidly to 137.5° (80 mm.), and between this temperature and 139° almost the entire quantity passes over.[1] The distillate is a colorless or very slightly

[1] The boiling-points of this oil are as follows: 114° at 20 mm., 120° at 39 mm., 135° at 69 mm., 137.5° at 83 mm.

yellow-colored oil, with a high refractive index and an ethereal odor somewhat resembling that of ethyl benzoate; *it does not react with phenylhydrazine, and instantly adds bromine in the cold* without liberating hydrobromic acid. Owing to the constant boiling-point and the further properties of this oil there seemed scarcely any doubt that a benzoic ester of β-allyl alcohol was present, but, nevertheless, the analyses (with the single exception of that of one of several preparations) indicated that this presumably uniform body was in reality a mixture:

	Calculated for $C_6H_5.CO_2.C.CH_3$ ‖ CH_2	For $C_6H_5.CO_2.C.CH_3$ | CH_3	For $C_6H_5.CO_2C_2H_5$.
C	74.07	73.23	72.00
H	6.17	7.36	6.66

	Found.			
	I.	II.	III.	IV.
C	73.63	72.92	72.86	72.66
H	6.09	7.76	7.84	7.93

These numbers, with the exception of those in the first analysis, agree with those which would be expected were a mixture of the benzoic esters of β-allyl alcohol, isopropyl alcohol and ethyl alcohol;[1] a separation by means of fractional distillation is, however, impossible, because the boiling-points of the substances in question lie too near together, as I proved by distilling in separate flasks isopropyl benzoate, ethyl benzoate, and the oil undergoing investigation, all at the same time and attached to the same manometer: the isopropyl ester boiled at 119°, the ethyl ester at 116°, and the product of the action of benzoyl chloride on acetone sodium at 120° (pressure 39 mm.). In order, therefore, definitely to determine the nature of the body under discussion I decided to saponify the oil and to identify the products formed by this means. Nine grams of the oil were mixed with a slight excess of 5-per cent. caustic potash solution (calculated for β-allyl benzoate) and then boiled for eight hours in a flask attached to an inverted condenser fitted with a mercury valve; after that time the ethereal odor had disappeared and the weight of oil diminished to 2 grams. The latter was separated from the alkaline solution, dried over

[1] Probably a trace of the product of the reduction of mesityl oxide, $C_{12}H_{20}O$ (boiling-point, 213°-217°), is also present; this would increase the proportion of hydrogen very much. No condensation-products of acetone are mixed with this oil, *for it does not react with phenylhydrazine.* Some analyses were obtained in which the hydrogen was as low as 7 per cent., but these are not given because, to make a perfectly fair representation, the above four sets of numbers were selected simply in the order in which the analyses were made.

potassium carbonate and fractioned. A few drops distilled between 120° and 134° and were evidently mesityl oxide; the thermometer then rapidly rose to 200°, between which temperature and 220° the whole of the remainder passed over. This high-boiling portion is identical in odor and other properties with the phoron which had previously been obtained; *it readily reacts with phenylhydrazine.* These condensation-products were evidently produced from acetone by the action of caustic alkali; the acetone, in turn, being the result of the saponification. That no such bodies were present in the original oil is abundantly proven by the fact that it does not react with phenylhydrazine, and further, by the vapor-density, which agrees quite closely with that predicted by theory.

Vapor-density of oil boiling at 114° (20 mm.), Hoffmann apparatus; vapor of aniline:

Weight of substance, 0.0442 gram, $V = 146$ cc., $h = 494.4$ mm., $t = 184.5°$, $h' = 76$ mm., $t' = 24°$, $B = 745$ mm. ($t = 18.5°$).

D — Calculated for $C_6H_5COOC(=CH_2)-CH_3 = 5.61$; Found $= 5.51$.

The alkaline solution left from this saponification was now acidified with dilute sulphuric acid, the precipitated benzoic acid filtered out and the acid solution supersaturated with potassium carbonate, distilled, the distillate treated in the same way, and so on until the separated organic liquid became anhydrous. No acetone was present in the substance so isolated, as was proven by the addition of sodium bisulphite; the liquid was therefore once more distilled over potassium carbonate, and finally dehydrated by repeated fractioning, with the addition of a small piece of sodium before each operation. The boiling-point was then 81.5° and the analyses as follows:

I. Twice distilled over sodium: C = 57.69, H = 13.29 per cent.

II. Three times distilled over sodium: C = 58.73, H = 13.3 per cent.

Calculated for $CH_3.CHOH.CH_3$: C = 60, H = 13.3 per cent.

Evidently a mixture of isopropyl alcohol and ethyl alcohol, similar to that obtained by acidifying acetone sodium, was present, and if it had been deemed necessary, the ethyl alcohol could have been entirely removed by continued distillations over sodium. This saponification proved, therefore, that the oil undergoing investigation was in reality a mixture of the benzoic esters of

isopropyl, ethyl and β-allyl alcohols; the acetone, which it was expected to isolate, was, however, converted into the high-boiling condensation-products of that body—in all probability the more easily because of its being liberated from its ethereal combination, as it were, in the nascent state. Although the mesityl oxide and the phoron which were obtained could have no other origin than the one referred to, it would nevertheless be more satisfactory to obtain the pure acetone by saponification, and in order to accomplish this result, hydrolysis by means of dilute hydrochloric acid was next attempted. Twelve grams of the oil, with an excess of 5-per cent. hydrochloric acid, were sealed in tubes and heated at 150° for forty-eight hours; the oil had then entirely disappeared and considerable pressure had been developed, as was shown on opening the tubes.[1] The acid liquid, after the benzoic acid had been removed, was supersaturated with potassium carbonate and then distilled, the distillate treated in the same way and so on, until the organic fluid, which was dissolved, was rendered anhydrous. *The entire quantity then boiled between* 60° *and* 85°. Two fractions of this liquid were taken, one boiling below and the other above 73°; the lower portion, which was about twice as great in volume as the other, was carefully treated with a saturated solution of sodium bisulphite, whereon the entire quantity solidified in the form of the characteristic shiny plates of acetone sodium bisulphite. Subsequently, pure acetone was obtained from this compound by heating with sodium carbonate. The liquid boiling above 73° also contained some acetone, but a large part was isopropyl alcohol mixed with a little ethyl alcohol. These results prove that by saponifying the neutral oil obtained by the action of benzoyl chloride on acetone sodium, *acetone*, isopropyl and ethyl alcohols can be isolated, in addition to benzoic acid. There can be no doubt, therefore, that acetone sodium, when treated with benzoyl chloride, yields a true ester of benzoic acid and that this ethereal salt is β-allyl benzoate, $C_6H_5COOC-CH_2$. The saponi-

$$\begin{array}{l} \\ \\ \\

If ordinary acetone in reality contains a carbonyl group, then the β-allyl alcohol changes to $CH_3—CO—CH_3$ as soon as it is liberated; but if, on the other hand, free acetone is an unsaturated alcohol, then no further change need be considered. I shall not, at the present time, commit myself to either opinion, as the work which I have undertaken with the hope of settling the constitution of acetone is not, as yet, completed.

The Portion of the Oil which is Soluble in Alkalies.

As was mentioned in the above, the ethereal solution which was obtained as a product of the action of benzoyl chloride on acetone sodium was successively treated with aqueous sodium bicarbonate, sodium carbonate and sodium hydroxide, and the yellow to red colored solutions so obtained were then each worked up separately. Benzoic acid is almost exclusively separated on acidifying the bicarbonate solution with dilute sulphuric acid, and indeed this substance is formed in such quantity that its production is, undoubtedly, an essential part of the entire reaction. It seems as if the quantity of benzoic acid is in direct proportion to the amount of mesityl oxide which is formed.[1]

The results with the sodium-carbonate solution are entirely different; when the latter is acidified there separates a red, semi-solid mass which yields *acetophenone*,[2] acetic acid and benzoic acid when it is distilled. It follows from this fact that ketones produced by the substitution of one or more hydrogen atoms in an acetone molecule by benzoyl chloride were present before distillation. The red precipitate which is obtained on acidifying with

[1] The formation of mesityl oxide is peculiar to this reaction with benzoyl chloride, but very little mesityl oxide is found in the substances isolated by direct acidification of acetone sodium, or in the products of reaction between that substance and ethyl chlorcarbonate. That the mesityl oxide is not due to the action of benzoyl chloride on the excess of free acetone is proven by the fact that the two substances can be left in contact for weeks with but very little condensation. When I first tried the action of benzoyl chloride on acetone sodium I extracted the ethereal solution with 10-per cent. sodium-hydroxide solution from the very beginning, and it then seemed to me as if the benzoic acid might be due to the saponification of an extremely unstable ester. However, the quantity of acid is as great if extraction with sodium bicarbonate is resorted to; it is always about 10 per cent. of the total quantity of benzoyl chloride (calculated in terms of benzoic acid) which was used. The benzoic acid also appears if no attempt is made to extract with alkalies, the ethereal solution being fractioned without further preliminaries, or if the same be distilled in a current of steam. In spite of all these considerations the most probable explanation seems to be that the benzoic acid is due to the saponification of an unstable ester.

[2] The acetophenone was separated by careful fractioning, as an oil boiling at 200°; it was identified by its characteristic odor, by a combustion, and finally by the formation of its compound with phenylhydrazine (melting-point 105°).

dilute sulphuric acid—in quantity it is about 8 grams for every 120 grams of benzoyl chloride used—was treated as follows, in order to isolate the substances contained therein: It was dissolved in the least possible quantity of 10-per cent. sodium-hydroxide solution, and carbon dioxide was then passed into the solution until no further precipitate separated. The resulting yellowish, flaky body was then filtered out and dissolved in the least possible quantity of hot absolute alcohol; when this solution is left for crystallization there separates a small quantity of fine, white needles, soluble in alcohol with difficulty, and melting at 213°.[1] These are filtered and the remaining mother-liquors allowed to stand. Long prisms then gradually form, and are separated when they no longer increase in quantity. They are then powdered, spread on a porous plate, and finally repeatedly recrystallized from the least possible quantity of alcohol. When entirely pure this body forms long, quadratic, needle-like prisms, which are soluble in alcohol, soluble with difficulty in ligroïn; when heated, they soften (if not entirely pure) at 78°, but do not melt until 100°–101° is reached. These properties agree completely with those found for dibenzoylacetone,[2] and analysis proved that the latter body is in reality produced:—

I. Substance, 0.1829 gram; CO_2, 0.5126 gram; H_2O, 0.0927 gram.

II. Substance, 0.1143 gram; CO_2, 0.3233 gram; H_2O, 0.0580 gram.

	Calculated for $C_{17}H_{14}O_2$.	Found. I.	II.
C	76.7	76.43	77.00
H	5.38	5.63	5.61

[1] This body is not very readily soluble in sodium carbonate, and it is therefore, in greater part, to be found in the high-boiling residue left in the retort after distilling the neutral oil. It will therefore be referred to again in a subsequent paragraph.

[2] Alexander B. Smith: Inaugural Dissertation, Munich, 1889, page 30. This author prepared dibenzoylacetone by the action of benzoyl chloride on sodium benzoylacetone. He ascribes the softening of the crystals at 78° to the presence of an isomeric body. I have found that dibenzoylacetone, if recrystallized a sufficient number of times, no longer softens at 78°; a body melting at 55° can, however, be separated from the last rests of the mother-liquors. The quantity of this substance which I have had at my command has been too little to allow me to hazard an opinion as to its nature. Whether it is an isomer of dibenzoylacetone, or whether it changes to ordinary dibenzoylacetone on recrystallizing, is yet to be determined. Claisen, in a paper (Ber. d. chem. Ges. **26**, 1879) which appeared while this article was being written, mentions that repeated crystallization changes the dibenzoylacetone (melting at 100°–101°) into an isomer melting at 109°–110°; I had not noticed this change with my dibenzoylacetone, even after recrystallizing nine or ten times. I have, however, as will be seen below, isolated another body which melts finally at 155°.

The crystals which were used in the first analysis changed the color of a solution of ferric chloride to an intense reddish purple; they probably, therefore, contained a trace of monobenzoylacetone, since this would decrease the percentage of carbon and increase that of the hydrogen.

The mother-liquors from the crystallization of dibenzoylacetone form a dark brown oil which possesses the very characteristic odor of monobenzoylacetone; if allowed to stand, part of this oil gradually solidifies, and the solid substance, when crystallized from 90-per cent. alcohol, deposits long needles having the characteristic appearance and odor of benzoylacetone. The melting-point of these crystals is 58° to 62°, and a comparison with a sample of benzoylacetone prepared by a different method [1] established their identity; the alcoholic solutions in both samples also assumed the same Bordeaux-red color when treated with a drop of a solution of ferric chloride. Owing to the very characteristic properties as well as to the difficulty with which the small quantities of benzoylacetone are to be separated from dibenzoylacetone, no ultimate analysis was made.

The High-boiling Residue which remains after distilling the Oil Insoluble in Alkali.

In spite of the fact that all of the alkali-soluble bodies have been removed before distillation, the residue which remains in the retort, and which is an almost black, tar-like mass, contains considerable quantities of benzoic acid, as well as some benzoylacetone. In order to remove these acid bodies the tar was once more dissolved in ether and then repeatedly extracted with 10-per cent. sodium-hydroxide solution; the ethereal solution was then dried over calcium chloride, the ether evaporated and the residue stood aside for possible crystallization. After some weeks a not inconsiderable quantity of a body which crystallizes in long, felt-like needles was deposited; this was separated from the remaining oil by being spread on a porous plate,[2] and was finally recrystallized from hot absolute alcohol. After this operation it became apparent that

[1] I owe this sample to the kindness of Prof. J. U. Nef, whom I wish to take this opportunity of thanking.

[2] I have found the dried pulp which is to be obtained from paper factories, and which is rolled in large sheets about ¼ of an inch in thickness, to be much superior to porous plates as an agent for removing sticky mother-liquors. The drying action is much quicker and more complete.

there were in reality two bodies present; the larger portion is with difficulty soluble in alcohol, and separates from the latter solvent in asbestos-like needles which melt at 214°, while the minor part separates from the mother-liquors as a granular precipitate which melts at 156° to 157.5°.

The body melting at 213° was repeatedly crystallized, and then finally dried at 100° and analyzed:

I. Substance, 0.0786 gram; CO_2, 0.2250 gram; H_2O, 0.0442 gram.

II. Substance, 0.1737 gram; CO_2, 0.4999 gram; H_2O, 0.0772 gram.

	Calculated for $C_{20}H_{18}O_3$.	Found. I.	II.
C	78.46	78.37	78.47
H	5.88	6.23	4.95

The body $C_{20}H_{18}O_3$ is in all probability obtained from benzoylacetone by the extraction of water, as the following equation will show: $2C_{10}H_{10}O_2 = C_{20}H_{18}O_2 + H_2O$; and it therefore may be dibenzoylmesityl oxide; whether it is formed from a sodium compound of mesityl oxide, or whether it is produced by condensation between two molecules of benzoylacetone, can naturally not be, as yet, decided.

In addition to the above there is found, as has been mentioned, another crystalline substance which is more soluble in alcohol, which separates from that solvent in short prisms having a melting-point of 156°–157.5°, and which gives the following numbers on analysis:[1]

Substance, 0.1715 gram; CO_2, 0.4767 gram; H_2O, 0.0014 gram.

	Calculated for $C_{17}H_{14}O_3$.	Found.
C	76.12	75.80
H	5.96	5.92

A body of the composition $C_{17}H_{16}O_3$ might be dibenzoylacetone after the addition of two hydrogen atoms, but all speculation as to whether such a substance is really under consideration would be premature at the present time.

The black, tar-like residue after all other substances have been separated shows no tendency toward further crystallization. It is decomposed on distillation, even in a vacuum, a large quantity of

[1] I could obtain enough of the pure body for only one analysis.

gas passing off, while benzoic acid and a trace of acetophenone distil over, leaving as a residue in the retort a perfectly solid resin. An attempt at saponification gave equally unsatisfactory results: benzoic acid and an uninviting neutral tar being produced, so that, as a consequence, further investigation was abandoned.

The experiments which have been detailed above show, without doubt, that acetone, like acetoacetic ether and other bodies related thereto, contains a hydrogen atom which is capable of being replaced by sodium, while the fact that acetone sodium forms an ester when treated with benzoyl chloride—to which ester the structural formula: $C_6H_5.COO.C\begin{matrix}CH_3\\ \| \\ CH_2\end{matrix}$ must be assigned—also proves, beyond doubt, that the sodium atom in acetone sodium is combined with oxygen to form a natroxyl group. It is possible, therefore, when dealing with the sodium compound of a strongly positive substance such as acetone, to substitute the sodium directly by benzoyl, an experience which is doubtless contrary to the one which has been made with acetoacetic ether. The formation of benzoylacetone from sodium acetone and benzoyl chloride can therefore be explained only by the assumption that addition must first take place.[1] The simultaneous production of dibenzoylacetone is, in my opinion, most easily understood by applying the explanation which Nef[2] gives in his paper discussing the similar reactions taking place with acetoacetic ether. The first change consists in the addition of benzoyl chloride:

$$\text{I.}\quad \begin{matrix}CH_3\\ |\\ CONa\\ \|\\ CH_2\end{matrix} + \begin{matrix}Cl\\ |\\ CO.C_6H_5\end{matrix} = \begin{matrix}CH_3\\ |\\ C\begin{matrix}ONa\\ Cl\end{matrix}\\ |\\ CH_2.CO.C_6H_5.\end{matrix}$$

The latter body now separates hydrochloric acid, leaving sodium benzoylacetone:

$$\text{II.}\quad \begin{matrix}CH_3\\ |\\ C\begin{matrix}ONa\\ Cl\end{matrix}\\ |\\ CH_2.CO.C_6H_5\end{matrix} = \begin{matrix}CH_3\\ |\\ CONa\\ \|\\ CH.CO.C_6H_5.\end{matrix} + HCl.$$

[1] The intense orange color which is produced as soon as benzoyl chloride comes in contact with sodium acetone may be due to the formation of such an addition-product.

[2] Ann. Chem. (Liebig) **266**, 61.

The liberated hydrochloric acid, of course, by preference will attack the acetone sodium, forming sodium chloride and free acetone; a lesser portion, however, also liberates benzoylacetone from its sodium compound. Sodium benzoylacetone is, however, also capable of adding benzoyl chloride:

III. $$\begin{matrix} CH_3 \\ | \\ CONa \\ \| \\ CH.CO.C_6H_5 \end{matrix} + \begin{matrix} \\ \\ Cl \\ | \\ CO.C_6H_5 \end{matrix} = \begin{matrix} CH_3 \\ | \\ C\!<\!\begin{matrix} ONa \\ Cl \end{matrix} \\ | \\ CH(CO.C_6H_5)_2, \end{matrix}$$

and the latter body, by again separating hydrochloric acid, leaves sodium dibenzoylacetone.

As sodium acetone has a structure represented by the formula $CH_3.CONa=CH_2$, it becomes highly probable that acetone is an unsaturated alcohol with the following composition: $CH_3—C.OH=CH_2$, and, in fact, many phases of the literature of this body, as well as some experiments which I am conducting in my laboratory, tend to show that such is really the case. I shall, however, defer this subject for a future communication after my present experimental work is completed, and shall also postpone until that time an extended discussion of my work on the action of chlorcarbonic ether, as well as of the action of carbon dioxide on acetone sodium.

In a former paper[1] I reported some experiments concerning the action of ethyl chlorcarbonate on acetone sodium. Further investigation has shown that the process is not at all as simple as the one which I then assumed to be the true one: several oils are formed which are extremely difficult to separate and which probably change their nature when distilled. By using phosphorus pentachloride as a reagent I have nearly succeeded in clearing up the investigation; a part of the work, however, is in need of further revision. In conclusion I wish to express my thanks to Messrs. D. M. Lichty and R. R. Putnam for their valuable assistance and active interest in carrying on this work.

August, 1893.

[1] This Journal **13**, 322.

REVIEWS.

DIE THERMODYNAMIK IN DER CHEMIE. Von J. J. VAN LAAR. Leipzig: W. Engelmann. (196 pp. Mark 7.)

The rapidly-growing interest of chemists in the problems and results of physical chemistry has created a need for a concise presentation of the thermodynamical theory of chemical processes, prefaced by an outline of the principles and methods of thermodynamics. This need the book by van Laar is intended to meet. In it are discussed successively the fundamental units; the first law; energy and entropy; van der Waals' theory of vapors (rather exhaustively); the $\partial \log K$ equilibrium-formulæ; and the recent theoretical work of Planck; together with varied applications in the theory of solutions of electrolytes. The treatment is of a decidedly mathematical character. J. E. T.

DIE LEHRE VON DER ELEKTRIZITAET. Von G. WIEDEMANN. IIte Auflage; Band I. Braunschweig: Vieweg. (1023 pp. Mark 26.)

The great extent of recent investigations in the subject of electricity has rendered necessary a new and rewritten edition of Wiedemann's monumental work. The first of its five volumes is now ready and the others are to follow in the near future. The book presents in organized form the results of all research-work in electricity up to the close of 1892, including a critical discussion of the material, and complete citations of the original papers—this making it invaluable as a reference-book in any branch of the subject. The present volume treats of the general properties of electricity, and the development of electricity in heterogeneous systems; including under the latter head all determinations of the conductivities of solutions, the corresponding experimental methods, the electromotive forces of different combinations, and a chapter on voltaic cells. J. E. T.